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Research paper

Investigation on microstructure and electrical properties of Bi doping $Ca_3Co_4O_9$ nanoparticles synthesized by sol-gel process

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Abstract

In this study, nanoparticles of Bi doped $Ca_{3-x}Co_4O_9$ [$Ca_{3-x}Bi_xCo_4O_9$ where x=0, 0.2, 0.4 and 0.6] were prepared by sol gel combustion method. The phase structures and microstructures of Bi doped $Ca_{3-x}Co_4O_9$ powders preparation were investigated. The microstructural observations of different Bi doped $Ca_{3-x}Co_4O_9$ powders were evaluated using X-ray diffraction analysis (XRD) and Variable Pressure Scanning Electron Microscope (VPSEM). The bulk $Ca_{3-x}Bi_xCo_4O_9$ samples were fabricated using uniaxial cold pressing technique. Electrical resistivity of bulk $Ca_{3-x}Bi_xCo_4O_9$ samples with different doping was measured using four-probe method from 300 to 700°K. The electrical resistivity was found to decrease with increasing temperature for the bulk $Ca_{3-x}Bi_xCo_4O_9$ samples. The electrical properties of $Ca_{3-x}Bi_xCo_4O_9$ are non-monotonic functions of x.

***Keywords**: Thermolectric; Calcium cobalt oxide; Electrical resistivity; Sol–gel; starch; Combustion; Nano-particles.*

1. Introduction

The thermoelectric generators could be an important part of the solution to today's energy challenge. The waste heat from automobiles, factories, and other similar sources totals to about 70% of the total primary energy produced, but is very difficult to reclaim because of the source amounts being small and widely dispersed. Thermoelectric materials and devices offer the only viable method of overcoming these problems by converting waste heat energy directly into useful electrical energy [1]. Thermoelectric devices recently attracted renewed interest in terms of their potential applications in clean energy conversion systems. Thermoelectric generators are consisted of intermetallic compounds, such as PbTe, Si-Ge and Bi_2Te_3. General applications like these kind of thermoelectric materials have been delayed, however, by special problems such as decomposition temperatures or low melting, scarcity or toxicity and expensive cost. Recently, ceramic oxide materials such as $Ca_3Co_4O_9$ have attracted attention as promising thermoelectric materials due to their potential to overcome the above mentioned problems.
The first widely studied member of the thermoelectric oxides family, $NaCo_2O_4$, was reported low electrical resistivity by Teraski et al. in 1997 wherein they demonstrated that this material exhibits a low electrical resistivity of 200 μΩ.cm at 300°K[2]. Recently, the intensive researches have been devoted to discovering a new oxide materials, in order to improve potential of thermoelectric properties and/or to develop thermoelectric systems for power generation [3, 4]. The sol–gel combustion method provides several advantages which are as follows: simple and economical preparation, easy control of homogeneity and stoichiometry. In this technique also, the reactant cations are intimately mixed on an atomic scale, so the rate of the reaction will be increased, leading to lower synthesis temperatures. Recently, oxides have attracted increasing interest as high temperature thermal materials for power generation using this type of processing methods according to their advantages. During the last decades, several studies of the thermoelectric materials using sol gel method such as $Ca_3Co_4O_9$[5-9], $Bi_2Al_4O_9$[10], $MgAl_2O_4$ [11], $NiFe_2O_4$[12], $CoZnFe_2O_4$ [13] and ZnO[14]. The aim of this investigation is to study the effect of Bi doped in $Ca_3Co_4O_9$ by using sol–gel auto-combustion method on the microstructural and electrical properties.

2. Experimental section

2.1. Materials and procedures

Polycrystalline samples of $Ca_{3-x}Bi_xCo_4O_9$ with X=0, 0.2, 0.4 and 0.6 were synthesized by the sol–gel combustion method using starch [$(C_6H_{10}O_5)n$] as a gelling agent and combustion fuel. The Calcium Nitrate Tetrahydrate $Ca(NO_3)_2{\cdot}4H_2O$ (99%, Sigma-Aldrich), Cobalt(II) Nitrate Hexahydrate $Co(NO_3)_2.6H_2O$ (99%, Sigma-Aldrich) and different amount from Bismuth(III) nitrate pentahydrate $Bi(NO_3)_3{\cdot}5H_2O$ (99%, Sigma-Aldrich) were dissolved in distilled water to obtain a mixed solution by using magnetic hot Plate Stirrer (IKA-C-MAG HS4, Germany). Local starch $(C_6H_{10}O_5)_n$ mixed with distilled water and the solution added slowly into the mixed metal nitrate solution. The resulting pink transparent solution was heated with constant stirring to the temperature in the range of 353-373 °K to obtain a pink gel. Afterwards, the resultant gel was decomposed at 673°K for 1 hr. using hot plate stirrer until changed that powder to black color. This powder was then heated to 1073 °K for 12 h to obtain $Ca_3Co_4O_9$ powder in order to remove the carbonaceous materials. $Ca_3Co_4O_9$ ceramic powder was pelletized using a hydraulic press technique employing a pressure of 5 ton, it compressed to form a pellet which was 15*15*3 mm in thickness then these pellets were sintered at 900 °C for 10 h.

2.2. Characterization of product

The crystal structure of $Ca_3Co_4O_9$ nanoparticles doped at different Al percentage were characterized by Rigaku (Smartlab) X-ray diffractometer with Cu-K_β radiation (λ= 0.13922 nm). The morphology of $Ca_3Co_4O_9$ nanoparticles were examined using Variable-Pressure Scanning Electron Microscope (VPSEM) Model-JEOL JSM-IT300LV. Electrical resistivity of $Ca_{3-x}Bi_xCo_4O_9$ with different doped of Bi were measured using the four-probe method equipment (DFP-03) with our modification. The thermoelectric properties electrical resistivity from 300 to 700°K was measured by means of a standard four-probe method using the 2400 Source Meter (KEITHLEY).

3. Results and discussion

3.1. XRD analysis

According to X-ray diffraction data, phase of $Ca_{3-x}Bi_xCo_4O_9$ (x = 0, 0.2, 0.4 and 0.6) nanoparticles synthesized by sol–gel auto-combustion method was obtained when Bi was substituted with Ca in that component are shown in Fig. 1. The similarity between the XRD patterns of undoped $Ca_3Co_4O_9$ and Bi doped $Ca_{2.8}Bi_{0.2}Co_4O_9$ powder suggest that the substituting ions of Bi do not change the crystalline structure. Afterwards, the x-ray diffraction patterns of the $Ca_{2.6}Bi_{0.4}Co_4O_9$ and $Ca_{2.4}Bi_{0.6}Co_4O_9$ powders started change (Fig. 1) and showed reflections with other phase like Co_3O_4 [15].

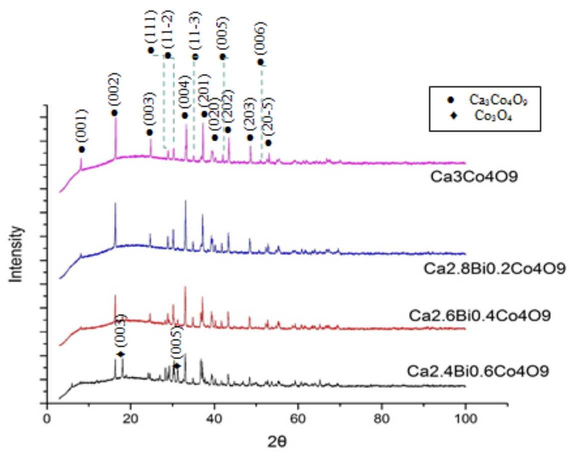

Fig. 1: XRD patterns of $Ca_{3-x}Bi_xCo_4O_9$ with various x value.

3.2. VPSEM micrograph analysis

The VPSEM images of ceramic prepared by the sol–gel combustion method with various Bi doping amount showed in Fig.2 (a-d). The samples showed micron-sized disk like grains which the average diameter is in the range of 0.3– 5 µm and there is obvious difference in the grain size and shape in these powders.

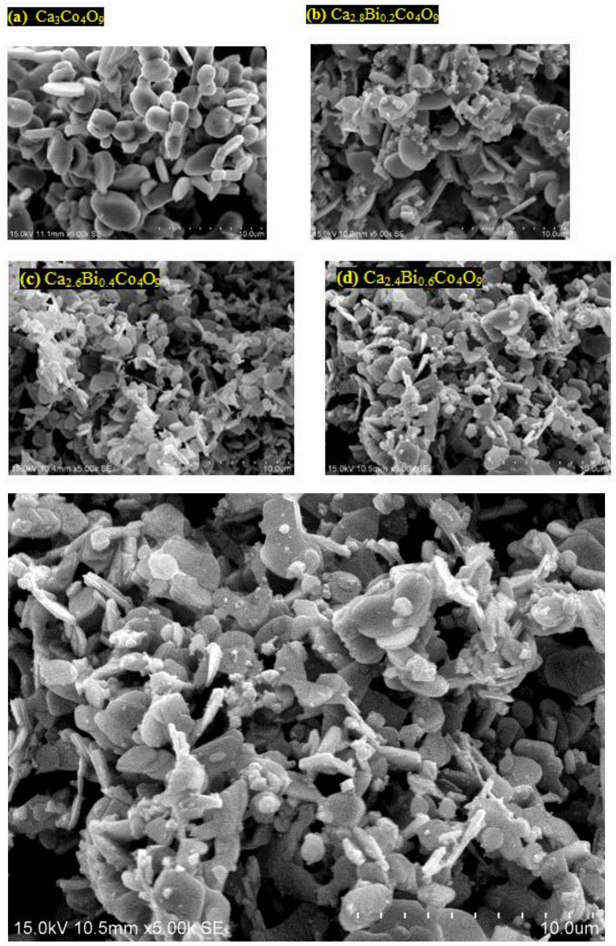

Fig. 2: VPSEM micrographs showing the morphology of $Ca_{3-x}Bi_xCo_4O_9$ powders with high magnification 5KX (a) x=0, (b) x = 0.2 (c) x = 0.4, and (d) x = 0.6

3.3 Electrical resistivity measurements

The pellets were used as a sample for electrical resistivity measurement by the four-probe method, applied current (I) and the resistance is measured in the temperature range of 300–700 K. The resistivity of the material is obtained from the following Eq. (1) [9]:

$$\rho = 2\pi S(V/I) \quad (1)$$

where S is the distance between probes 2.5mm, V is the obtained voltage across the two inner contacts, and I is the current passing through the sample.

Fig. 3 shows the relation between electrical resistivity of material with increasing temperature. $Ca_3Co_4O_9$ p-type semiconductor must have a narrower band gap so that an appreciable number of charge carriers are in the valence and conduction bands at room temperature. When the temperature increased, the thermal agitation increases and some valence electrons gain energy greater than activation energy (Ea) and then jump to conduction band. A similar trend was reported by researchers, where they observed an increase in the electrical conductivity on doping elements in the $Ca_3Co_4O_9$ [15-18]. The increases in the ρ value with Bi content were qualitatively explained by changes in the hole carrier concentration. As more Bi^{3+} ions replace Ca^{2+} ions, the hole carrier concentration of $Ca_3Co_4O_9$ decreases, leading to an increase in ρ. When the amount of Bi addition to $Ca_3Co_4O_9$ is too small (x = 0.2) to significantly affect the carrier concentration, the value ρ decreases, which can be used to enhance the thermoelectric performance of $Ca_3Co_4O_9$.

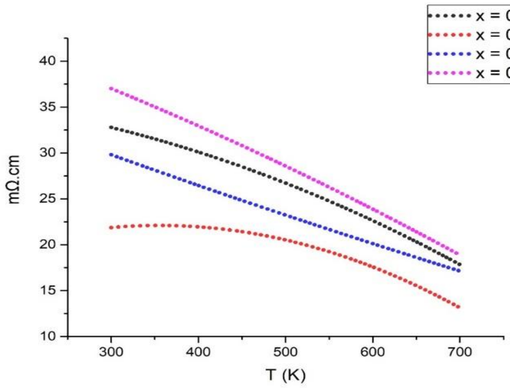

Fig. 3: Electrical resistivity as a function of temperature for $Ca_{3-x}Bi_xCo_4O_9$.

3. Conclusions

The effect of Bi doping on the microstructural and electrical properties of $Ca_{3-x}Bi_xCo_4O_9$ nanoparticles have been studied in this investigation using sol-gel combustion method. The XRD study confirms the formation of $Ca_3Co_4O_9$ structure. The structure remains intact even doping with x= 0.2 Bi concentration. Afterwards, the new phase (Co_3O_4) begins to form after adding Bi more than x=0.2. The electrical properties of $Ca_{3-x}Bi_xCo_4O_9$ are non-monotonic functions of x. The electrical resistivity of $Ca_3Co_4O_9$ nanoparticle is observed to be reduced until x=0.2 Bi-doping with different temperature. The lower electrical resistivity's (22 and 12.9 mΩ.cm) of $Ca_{3-x}Bi_xCo_4O_9$ are obtained in x = 0.2 between 300 and 700°K respectively indicates a material that readily allows the flow of electric current. The semiconducting behavior of the $Ca_{3-x}Bi_xCo_4O_9$ nanoparticles is confirmed by the decreasing electrical resistivity with temperature.

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