



Mechanochemically assisted solid-state and citric acid complex syntheses of Cu-doped sodium cobaltite ceramics



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ABSTRACT

In the last decade, the sodium cobaltite ceramic became a promising candidate for potential thermoelectric applications, because of its large thermopower and low resistivity. In this work, polycrystalline samples of $\text{NaCo}_{2-x}\text{Cu}_x\text{O}_4$ ($x = 0, 0.01, 0.03, 0.05$) were prepared using mechanochemically assisted solid-state reaction method (MASSR) and the citric acid complex method (CAC). Bulk samples were prepared by pressing into disc-shaped pellets and subsequently subjected to a thermal treatment at 880 °C in inert argon atmosphere. Changes in structural and microstructural characteristics of the samples, caused by the substitution of Cu for Co, were characterized using X-ray diffraction (XRD) analysis, and scanning electron microscopy (SEM), respectively. The results of inductively coupled plasma (ICP) analysis showed that the compositions of the final products correspond to $\gamma\text{-NaCo}_2\text{O}_4$ and confirmed that desired compound was obtained in both syntheses procedures. The advantages and disadvantages of these two syntheses procedures have been observed and discussed: the CAC method enabled obtaining samples with higher density and fine microstructure compared to the MASSR method, thus better thermoelectric properties. The Cu^{2+} substitution led to the increase in Seebeck coefficient in both synthesis routes. The highest figure of merit of 0.022 at 300 K was observed for the sample doped with 1 mol% Cu, obtained by the CAC method, and it was almost twice higher than in the undoped sample confirming the significant influence of Cu-doping with even small concentrations.

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1. Introduction

The waste thermal energy created as a byproduct of industrial processes and working machinery from cars, factories, and power plants can be converted into electric energy based on the thermoelectric effects [1]. The thermoelectric performance of a material is expressed by the dimensionless figure of merit (ZT), as $ZT = S^2T/\rho\kappa$, where ρ , S and κ are electrical resistivity, Seebeck coefficient (also called thermopower) and thermal conductivity, respectively [2]. Ratio S^2/ρ known as the power factor, determines the electrical properties. It is necessary that the good thermoelectric material possesses large power factor and low thermal conductivity. These properties are related, so it is difficult to control them independently. Large S will not always give rise to high ZT , so

among the competing effects, the most important is to obtain a high figure of merit.

The thermoelectric materials such as Bi_2Te_3 and PdTe contain toxic heavy elements and must be protected from the oxidation. So, there is a request for environmentally friendly, non-toxic materials with good thermoelectric properties [3]. Some conductive oxides, such as $(\text{Zn}_{1-x}\text{Al}_x)\text{O}$, $(\text{Ca}_2\text{CoO}_3)_x\text{CoO}_2$ and $\text{Na}_x\text{Co}_2\text{O}_4$, have been suggested as potential thermoelectric materials [4–6].

In the past years, much attention has been paid to NaCo_2O_4 , that belongs to the alkali ternary oxide group, A_xMO_2 ($\text{A} = \text{Na}, \text{K}; \text{M} = \text{Cr}, \text{Mn}, \text{Co}$, etc.), because of its interesting structural and transport properties [7]. This oxide has a hexagonal layered structure with $\text{P6}_3/\text{mmc}$ space group symmetry, and it consists of conductive CoO_2 layers and insulating Na layers alternately stacked along c -axis [7,8]. The CoO_2 layers are consisted of tilted CoO_6 octahedrons, which share edges with the nearest octahedrons within the same CoO_2 layer. As a consequence, oxygens and cobalt are not in the same plane. Two adjacent CoO_2 layers are tilted in the opposite direction (Fig. 1).

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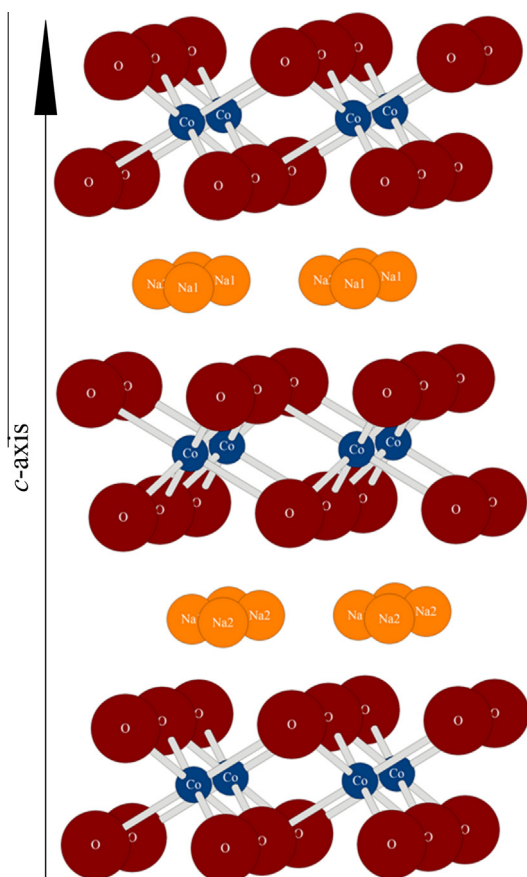


Fig. 1. Crystal structure of γ - NaCo_2O_4 .

The CoO_2 layers possess highly correlated electrons and are responsible for the electronic conduction, while sodium ions work only as a charge reservoir and serve as regions for phonon scattering. Very important feature is that sodium ions randomly occupy 50% of the regular sites in the sodium layer which makes it almost like a glass for the in-plane phonons [9]. Assembling these two types of layers into superlattice, each of them will have its own function and consequently can be independently controlled, thus, thermoelectric performance can be upgraded [10,11]. Sodium stoichiometry is variable, and depending of the sodium content, it has been reported three types of crystal structure of $\text{Na}_x\text{Co}_2\text{O}_4$, P3: β - $\text{Na}_x\text{Co}_2\text{O}_4$ ($1.1 \leq x \leq 1.2$), P2: γ - $\text{Na}_x\text{Co}_2\text{O}_4$ ($1.0 \leq x \leq 1.4$) and O3: α - $\text{Na}_x\text{Co}_2\text{O}_4$ ($1.8 \leq x \leq 2.0$), and the P2-type shows the largest thermoelectric power in spite of its metallic conductivity [10].

Incorporation of dopants into the layered oxides improves the thermoelectric properties. Substituting cobalt with copper in sodium cobaltite improves the thermoelectric properties of $\text{NaCo}_{2-x}\text{Cu}_x\text{O}_4$, for $x = 0.1, 0.2, 0.3$ and 0.4 [12,13] but in these samples secondary phases such as Co_3O_4 , NaCoO_2 , Na_2CO_3 , CuO , NaCuO and NaCu_2O_2 were present. Concerning this, our idea was to investigate $\text{NaCo}_{2-x}\text{Cu}_x\text{O}_4$ ($x = 0, 0.01, 0.03, 0.05$), to avoid the formation of secondary phases and to examine the effect of small concentration doping on the thermoelectric performance. Although sodium cobaltite is promising thermoelectric material the scientists deal with the problems during the synthesis and the sintering of this material. First of all, in the conventional solid-state reaction method, sodium cobaltite can be obtained only after several temperature treatments in the temperature range of 800–930 °C [14–18]. Also, Na tends to evaporate at high temperature, therefore long time synthesis can ruin stoichiometry changing the material composition. In order to solve these problems it is necessary to

reduce synthesis temperature and improve mixing of the precursors using alternative synthesis methods, such as mechanochemical and sol-gel synthesis methods.

Mechanical activation of the solid materials induces several processes: reduction of particles size and increase of surface area, deformation of the crystalline structure of solids, phase transformations and chemical reactions due to the heat generation [19]. The most important by this method is that it enables increasing of reaction rates and lowering of reaction temperatures of milled powders [20]. Beside the direct synthesis of a metastable material, high energy ball milling can be used for powder pre-treating and modifying conditions for the solid state synthesis. Previously, high energy ball milling and post firing was used for preparation of powder Na_xCoO_2 which is used as a cathode for battery application [21].

On the other hand, the citric acid complex method, as a chemical solution process, enables mixing of the constituents at the atomic level by forming metal citrate complexes, which results in increased reaction rate and lower synthesis temperature. It was expected to obtain homogeneous, fine powders, and therefore, developed fine microstructures in the sintered body with high density of the compacts [22,23].

Having all this in mind, we applied mechanochemically assisted solid-state reaction method and the citric acid complex method in order to promote the reaction and time necessary for obtaining sodium cobaltite. Subsequently, we used reaction sintering process and obtained dense ceramic at lower temperature with preserved sodium stoichiometry. The aim of this study was to investigate the effect of the small amounts of Cu as dopant on the thermoelectric properties of sodium cobaltite and to elucidate the advantages and disadvantages of these syntheses procedures.

2. Experimental

Polycrystalline samples of $\text{NaCo}_{2-x}\text{Cu}_x\text{O}_4$ ($x = 0, 0.01, 0.03, 0.05$) were prepared by mechanochemically assisted solid-state reaction method, between sodium carbonate (Na_2CO_3 , Sigma Aldrich, 99.95–100.05%), cobalt(II,III) oxide (Co_3O_4 , Sigma Aldrich, 99.8%) and copper(II) oxide (CuO , Sigma Aldrich, 99%), and denoted as NCO-MASSR, NCO1-MASSR, NCO3-MASSR and NCO5-MASSR. An excess of Na_2CO_3 is added to compensate the volatility of sodium. Each powder mixture was mechanically activated by grinding for 3 h in a planetary ball mill (Fritsch pulverisette 5) with a ball to powder mixture ratio 20:1, at the basic disc rotation speed of 360 rpm. The powder was then compacted into the pellets under a pressure of 590 MPa. The green compacts were subjected to a reaction sintering process at 880 °C for 24 h with the heating and the cooling rate of 5 °C/min in argon atmosphere, to avoid contamination by moisture.

Sodium acetate (NaCO_2CH_3 , Alfa Aesar, 99%), cobalt(II) acetate tetrahydrate ($\text{Co}(\text{CO}_2\text{CH}_3)_2 \cdot 4\text{H}_2\text{O}$, Alfa Aesar, 98%), copper(II) acetate monohydrate ($\text{Cu}(\text{CO}_2\text{CH}_3)_2 \cdot \text{H}_2\text{O}$, Sigma Aldrich, 99%) and citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, Lachner, 100.05%) were used as starting components for the citric acid complex procedure. Stoichiometric amounts of the metal salts were added to the citric acid aqueous solution and dissolved by heating and stirring. The citric acid to the metal cation molar ratio was 3:1. An excess of sodium acetate was used in order to obtain the final composition of $\text{NaCo}_{2-x}\text{Cu}_x\text{O}_4$ ($x = 0, 0.01, 0.03, 0.05$). These samples were denoted as NCO-CAC, NCO1-CAC, NCO3-CAC and NCO5-CAC. The mixture was gradually heated up to 140 °C and during this heating process, the solution condensed and chelating process was promoted. The obtained viscous product was further heated at 450 °C for 2 h until the dark mass precursor was formed and finally calcined at 800 °C for 20 h in inert argon atmosphere. The calcined powder was compacted into the pellet at 390 MPa, and the final product was obtained after sintering at 880 °C for 20 h in argon atmosphere. The same procedure was repeated for all compositions.

The thermal analysis of homogenized and mechanically activated powder mixture and dark mass precursor obtained by the citric acid complex method of undoped and Cu-doped sodium cobaltite was carried out using a differential thermal/thermogravimetric analysis (DT/TGA) in the temperature range from room temperature up to 1100 °C and 1000 °C, respectively, at a heating rate of 10 °C/min in the nitrogen atmosphere (SDT Q600 TA). The crystal structure of the thermally treated samples was analyzed with X-ray powder diffraction (XRD, Rigaku RINT 2000) using Fe K α radiation as an X-ray source, ($\lambda = 1.93604$ nm), and the lattice parameters were calculated according to the XRD patterns. The morphology of the powders was examined using JEOL JSM-7600F field emission scanning electron microscope (FE-SEM) and the microstructure of the sintered samples was

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