High Thermoelectric Performance Of Unsintered $NaCo_2O_4$ Nanocrystal

Mehmet OkanErdal, Mustafa Koyuncu, İbrahim Uslu

Abstract: Sodium cobaltite ($NaCo_2O_4$) nano crystalline thermoelectric materials were obtained using electrospinning technique. Electrospunnanofibers was calcined at 800 °C and sintered at 850 °C in open air atmopshere. We have investigated the microstructure and thermoelectric properties of the sintered and unsintered samples for analysis sintering effect. The calcined sodium cobaltite crystal structures were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Products molded by cold pressing method, and one of the pellets were sintered at 850 °C by conventional sintering, the other not subjected to the sintering process. Thermoelectric properties of the both materials were measured by PPMS system in the temperature range 10-300 K. The dimensionless figure of merit (ZT) values at 300 K is $4 \times 10^{-5}$and 9×10^{-5} for sintered and unsintered samples respectively. Although conventional sintered technique increase thermoelectric power and thermal conductivity approximately % 50 but it 4-fold decreased electrical conductivity.

Index Terms: Thermoelectric properties, Sodium Cobal OxideNanocrystalline, Electrospinning.

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1 Introduction

THERMOELECTRIC is a generic name given to the event the conversion of heat energy directly into electrical energy or vice versa. This idea is very valuable in today's world which is rapidly increasing energy consumption. Thermoelectric energy conversion is considered to be the energy source of the future. A high performance thermoelectric material must have high thermoelectric power, electrical conductivity and, low thermal conductivity [1]. However, requirements for high-efficiency thermoelectric materials are not easily satisfied since these three parameters are interrelated [2], [3]. In recent years, different approaches have been used for improving the thermoelectric efficiency. The idea of using nanotechnology to further improve conventional thermoelectric materials has led to many exciting results to increase the electrical conductivity or to decrease the thermal conductivity [4], [5], [6].In addition, the molding and sintering technique is also very important for the yield of good thermoelectric material production [7], [8], [9], [10]. In recent years, Polymeric precursor such as poly vinyl alcohol (PVA) have been researched in thermoelectric devices recently due to solution-process-based fabrication, such as electrospinning, spin coating, and inkjet printing [11], [12]. It is found that long chain polymers have a substantial effect on the electrical conductivity. Also, the thermal conductivity of polymer increases with the increase of polymer chain length as has been shown by Zhao et al. [13]. In this study PVA polymeric precursor is used to prepare nanocomposite powders that, when sintered, convert to pure Sodium–cobalt oxide ($NaCo_2O_4$). It has been revealed that $NaCo_2O_4$ has potential as a thermoelectric material [2],[14], [15], [16] because of the sodium cobaltite have high Seebeck coefficient, low resistivity and low thermal conductivity. Since $NaCo_2O_4$ is a ceramic material it can be used at high temperatures without deterioration of their performance due to oxidation [17], [18].

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2 Experimental Details

In this study, PVA (average molecular weight of 85 000-124000 g/mol) was obtained from Sigma Aldrich and sodium and cobalt acetate was obtained from Merck. Deionized water was used as a solvent. Aqueous PVA solution (10%) was first prepared by dissolving PVA powder in distilled water and heating at 80 °C with stirring for 3 h, then cooling to room temperature. Sodium and cobalt acetate solutions were added to the aqueous PVA at 60 °C separately and drop by drop and the solution was vigorously stirred for one hour at this temperature. Stirring was continued for 2 h at room temperature. Thus, a viscous gel of PVA/Na-Co acetate solution was obtained. The polymeric solution was first transferred to a 50 mL syringe, which was connected to a capillary needle with an inside diameter of 0.8 mm. A copper electrode was attached to the needle, a DC power supply produces 35 kV against a grounded collector screen distant 15cm. With the syringe pump set at 2 mL/h, the electric force overcomes the surface tension of the solution at the capillary tip, and a jet emerges. Nanofibers wascalcined at 800 °C for 12 h in atmospheric conditions and these powders was pelleted under 5000 MPa of pressure. The pellet samples was sintered at 850 °C for 12 h in atmospheric conditions.

3 Measurement and Characterization

Composite morphology was taken by scanning electron microscopy JEOL JSM 7000 on the samples sputtered with gold and observed at an accelerating voltage of 20 kV. SEM micrographs of the electrospun PVA/(Co–Na) acetate nanofibers, nanopowders and surface of pellets are presented in Fig 1,

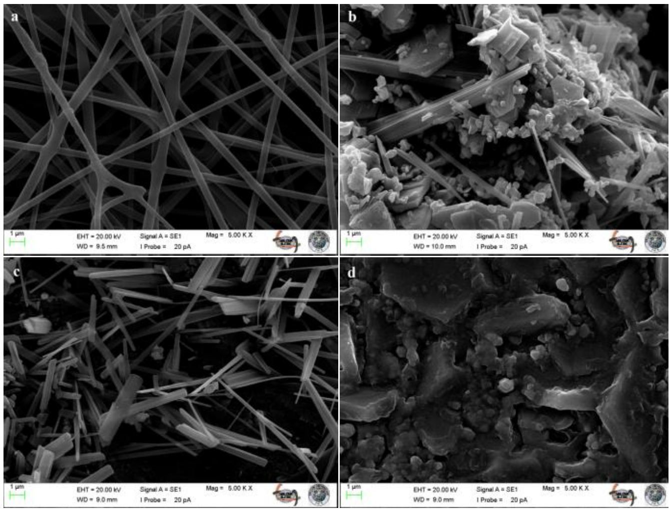

Fig. 1*.SEM micrographs; a nanofiber ; b. after calcination; c. after molding and d. after sintering.*

As it is seen from the SEM images, the average fiber radius is calculated as 300 nm. Droplet formation and aggregation was not observed in the structure. The SEM micrograps of the $NaCo_2O_4$nanocrystalline ceramics are given in Figure 1. b. The nano ceramic composite exhibited a unique microstructure in which nano rod and plate-like grains were observed with 150 nm thickness. The SEM micrograps of the unsintered $NaCo_2O_4$ pellet are given in Figure 1. c. As seen nanorod structures has become apparent outer surface. It is clearly observed from the SEM micrographs in Figure 1. d., nanorods was completely lost in the outer surface of the sintered samples. It is clearly seen on the external surface that the layers are fused into other one. Also ends of nano rod can still be determined.

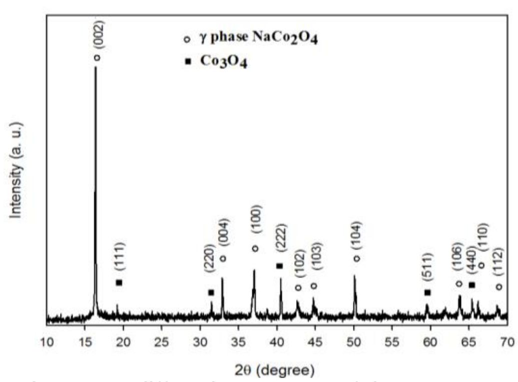

Fig. 2*The X-ray diffraction pattern of the nano crystalline ceramic.*

The structural analysis of the ceramic composite was performed by X-ray diffraction (XRD) and the results can be seen in Fig. 2. Powder XRD patterns were measured on a GND APD 2000 Pro X-ray diffractometer using graphite monochromotor and Cu source ($K\alpha1$=1,540598 Å; $K\alpha2$=1,54439 Å) operated at 40 kV and 30 mA and the patterns were collected at a scanning speed of 1.0 degree (2θ) per minute with a 0.02 degree step in the 2θ range 10-70 degree.The sharp peaks seen in the Figure 3 suggest that the obtained samples predominantly γ-phase $NaCo_2O_4$[19], [20], [21]. The crystal structure of sintered nanofibers sample is monoclinic and its cell parameters a = 29.2200 Å, b= 9.4800 Å, and c= 13.5100 Årespectively. The X-ray results also exhibit that there are relatively small amounts of Co_3O_4 present in the samples which is probably due to sodium evaporation during the calcination process at 850 °C[22].

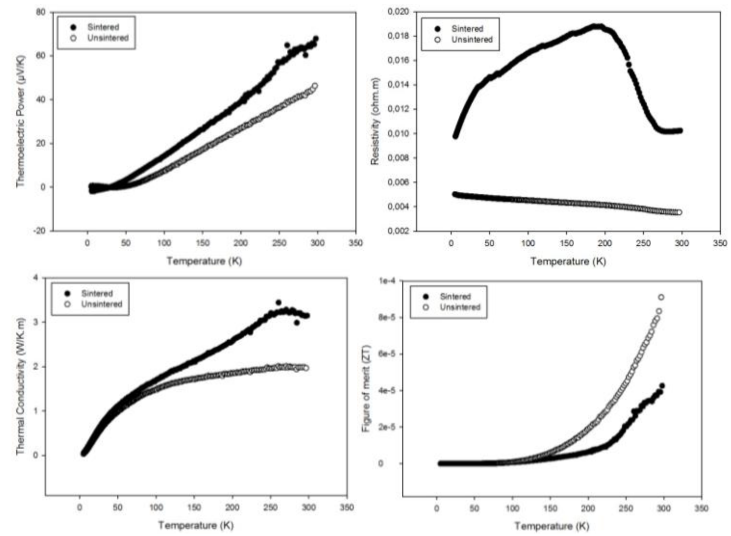

Fig. 3 *Thermoelectric properties of $NaCo_2O_4$*

- ***a.*** *ThermoelectricPower - Temperature*
- ***b.*** *Resistivity – Temperature*
- ***c.*** *ThermalConductivity – Temperature*
- ***d.*** *Figure of Merit – Temperature*

Thermoelectricproperties of sodiumcobaltitenanocristallineceramicwasmeasuredby Lot-OrielPhysicalPropertiesMeasurementSystem (PPMS) in the temperature range 10-300 K. These results can be seen in Figure 3. It is clearly observed from the Fig. 3, the unsintering pellet at 300 K, ρ, κand S of thewhiskersare 0,0035 ohm.m, 1,98 W/K.mand 46,5 μV/K respectively. Forsinteredpellet at thesametemperatureρ, κand S of thewhiskersare 0,01 ohm.m, 3,14 W/K.mand 67,8 μV/K respectively.Sintering process increased thermoelectric power, thermal conductivity and electrical resistivity values. ThecalculateddimensionlessFigure of Merit (ZT) at thistemperatureshowsrecordvalue of $9x10^{-5}$and $4x10^{-5}$respectively. The figure of merit of unsintered sample is more than twice the sintered samples.

4 Conclusion

In this study, p-type stable and thermoelectrically active nanocomposite material has been successfully synthesized for experience of sintering effect.The obtained thermoelectric values are consistent with literature data [7], [8], [9],10].It is clearly seen that the Fig. 3, thermoelectric properties of sintered and unsintered materials are very different. The sintering process increased the thermoelectric power while the electric conductivity is greatly decreased. Similarly, the sintering process increased the thermal conductivity but this situation is undesirable for the thermoelectric figure of merit. After the sintering process, nanorod-like structures has been disappared and their super extra electronic properties are lost and the intensity of the desired properties of the material decreased. Nanostructures has led to improved electrical conductivity and also led to the reduction of thermal conductivity due to the porosity of these structures. In addition to, sintering process has also led to a reduction in surface area. We believe that this effect needs to be investigated and studied in detail.

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