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Resistivity and Thermoelectric Properties of Na_xCoO_2 (x = 0.65 - 0.75)

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ABSTRACT

We have investigated the temperature dependence of electrical resistivity and thermoelectric power of polycrystalline samples of Na_xCoO_2 with x = 0.65, 0.7 and 0.75. The powder x-ray diffraction pattern reveals that the present system belongs to hexagonal unit cell with lattice parameters a = 2.834 Å and c = 10.821 Å. For all samples, both resistivity and thermoelectric power increase with temperature. The positive temperature coefficient of resistivity ($d\rho/dT > 0$) indicates that the samples are metallic in nature up to 300 K. With increasing x, resistivity decreases whereas thermoelectric power increases and as a result the power factor enhances vary rapidly. The large value of power factor at 300 K indicates that Na_xCoO_2 can be a very promising material for the use in high-temperature thermoelectric power generation devices.

KEYWORDS: Electrical resistivity, Thermoelectric power, Thermoelectric device

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INTRODUCTION

A thermoelectric device is a device that converts heat into electrical energy through the thermoelectric power (Q) of solids. Thermoelectric devices can be used for heating or cooling purposes, or for power generation. There are vast applications of thermoelectric devices in industries and one such promising application is the waste-heat energy harvesting in automotive industry. Remote space missions also use thermoelectric devices for power generation. The main challenge remains to enhance the performance of thermoelectric devices which can be very much efficient, since there is no theoretical upper limit of Q. Another important factor is that the lifetime of the device can be as long as the lifetime of the material from which the device is made. More importantly the device should be environmentally friendly in the sense that it produces no waste matter. To become a good thermoelectric material large thermoelectric power and low electrical resistivity (ρ) are required. One can quantify the efficiency of thermoelectric material in terms of power factor (Q^2/ρ)[1,2]. For good thermoelectric materials, power factor should be large.

The layered sodium cobaltate Na_xCoO_2 has been studied due to its good thermoelectric response[3,4,5,6]. Because of high electrical resistivity, the oxides are thought to be poor thermoelectric materials but the compound Na_xCoO_2 proved it otherwise. The magnetic structure of the compound is reported to be complex and the exact arrangement of the Co spins is yet unclear. Here we report the transport properties of Na_xCoO_2 with x = 0.65 - 0.75. We have measured the resistivity and thermoelectric power of the samples as a function of temperature[5,6,7,8].

MATERIALS AND METHODS

Polycrystalline samples of Na_xCoO_2 with x = 0.65 and 0.7 were prepared by standard solid-state reaction technique by using Na_2CO_3 and Co_3O_4 in stoichiometric proportions. The heating procedure was basically rapid heat-up technique in which the mixed powders were put directly in a preheated furnace at 750°C and fired for 24 h. The heated powders were reground and calcined at 850°C for 15 hours in oxygen. To reduce the Na loss, the mixture was put in a preheated furnace. The samples were characterized by powder x-ray diffraction (XRD). Samples for powder XRD were prepared by grinding the samples and pressed on a glass holder to achieve a smooth flat surface. We have measured the diffraction data by using the diffract meter in reflection mode. Using a automated goniometer, step by step scattered intensity has been measured.

The electrical resistivity of the samples was measured by using standard four probe technique. The four probes are four thin copper wires, which were connected to the rectangular-shaped sample using silver paint contacts. The current is made to flow between two outer probes and voltage is measured between two other inner probes. The contacts were usually made at room temperature but the painted samples were heated at 150-200 ^{0}C for 15 minutes to reduce the contact

resistance. For the temperature variation of the sample, a closed-cycle helium refrigerator was used. Sample temperature was controlled by using a temperature controller. To measure the sample temperature accurately, one end of a chromel-alumel thermocouple was placed very near to the sample. A dc current was sent through the sample from a constant current source and the voltage across the sample was measured by using a nanovoltmeter. The signals from the voltage probes and thermocouple are recorded as resistance (R) and temperature, respectively by the computer. The resistivity of the sample can be calculated as $\rho = Rl / A$, where A is the cross sectional area and l is the length of the sample *i.e*. the distance between two inner probes.

There are two basic techniques for the measurement of thermoelectric power Q. One is integral and another is differential technique. In the integral method, one end of a rather long wire specimen is held at a fixed temperature and the other end is heated to a temperature T, where T can vary through the temperature range of interest. The thermo-emf $V(T)$ of the thermocouple formed by the specimen and reference wire is measured. The thermoelectric power of the couple is given by $Q(T) = \mathrm{d}V(T) / \mathrm{d}T$. However, for polycrystalline or single crystal samples it is necessary to measure $Q(T)$ with the differential method in which rather short bar-type specimens are used. In this method, a small temperature gradient δT is maintained across the specimen which gives rise to a thermo-emf δV and the thermoelectric power of the couple is given by $Q(T) = \delta V(T) / \delta T$. For this relation to be valid, the temperature difference across the specimen must be small enough so that $Q(T)$ curve is not smeared out, the specimen must be homogeneous and the temperature must be uniform in the vicinity of connections between dissimilar metals in the measuring circuit.

RESULTS AND DISCUSSION

Figure 1 shows XRD pattern of Na_xCoO_2 for x = 0.65. Almost all the peak positions are indexed with hexagonal unit cell of the space group $P63/mmc$. The lattice parameters obtained from the Rietveld refinements are a =2.834 Å and c =10.821 Å, which are comparable with reported values. The temperature profile of electrical resistivity of Na_xCoO_2 for different x is displayed in figure 2 (a). For x = 0.65, the value of resistivity at 15 K is around 0.5 mΩ-cm which increases almost linearly with temperature and becomes ~ 4 mΩ-cm at 300 K. With increasing Na concentration, resistivity does not change appreciably below 30 K but above that resistivity starts to decrease and the decrement becomes much more prominent with increasing temperature, i.e., the temperature coefficient of resistivity ($\mathrm{d}\rho/\mathrm{d}T$) diminishes with x. Also the room temperature resistivity decreases very rapidly with Na concentration (ρ ~ 4 mΩ-cm for x = 0.65 and ρ ~ 2 mΩ-cm for x = 0.75). So it is clear that all samples exhibit metallic behavior in the temperature range 15 K – 300 K.

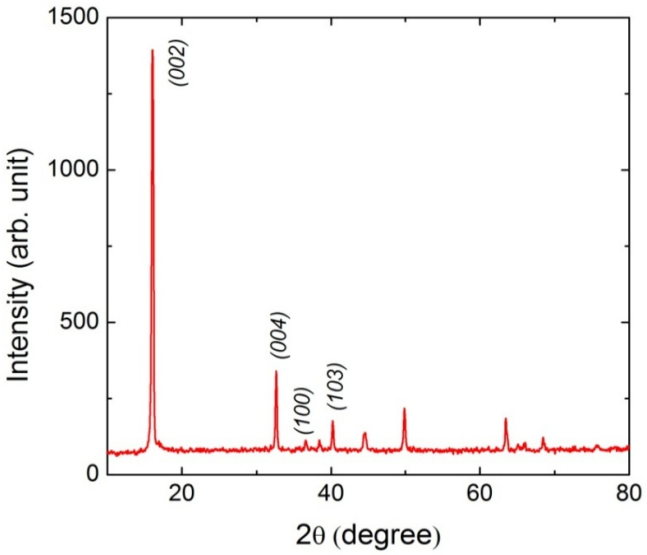

Figure. 1 – Powder x-ray diffraction pattern of Na_xCoO_2 with x = 0.65.

For x = 0.75, the sample exhibits a constant d ρ/dT in the temperature range 50-300 K but below 50 K, the value of d ρ/dT is increased, demonstrating changed conduction process below this temperature. Basically the change of the slope of $\rho(T)$ curve represents the magnetic transitions around the temperature 20 K. From detailed magnetization measurements, some groups have already reported that there is a magnetic transition around 21 K. Figure 2 (b) shows the temperature dependence of thermoelectric power of Na_xCoO_2 for different x. For x = 0.65, Q increases with temperature but there is a kink at around 230 K. With increasing x, thermoelectric power increases and the kink shifts towards the lower temperature. At room temperature, the value of Q is around 80 μV/K x = 0.65 and becomes ~ 140 μV/K x = 0.75. For a good thermoelectric material, apart from large thermoelectric power and low electrical resistivity, the power factor is an important parameter to determine the efficiency of thermoelectric device. We have estimated the value of power factor, Q^2/ρ at room temperature (~ 300 K) for different Na concentration which is shown in figure 3. It is clear from figure 3 that power factor increases very rapidly with increasing Na concentration and attains a value 1.01 $mWm^{-1}K^{-2}$ for x = 0.75, indicating that the present material can be considered as a good thermoelectric material. Here, I would like to mention that although Q is not so sensitive to grain boundaries effect in oxide materials, ρ is extremely sensitive to the presence grain boundary. So in case of single crystals, resistivity becomes much lower and as a result power factor *would* become very high.

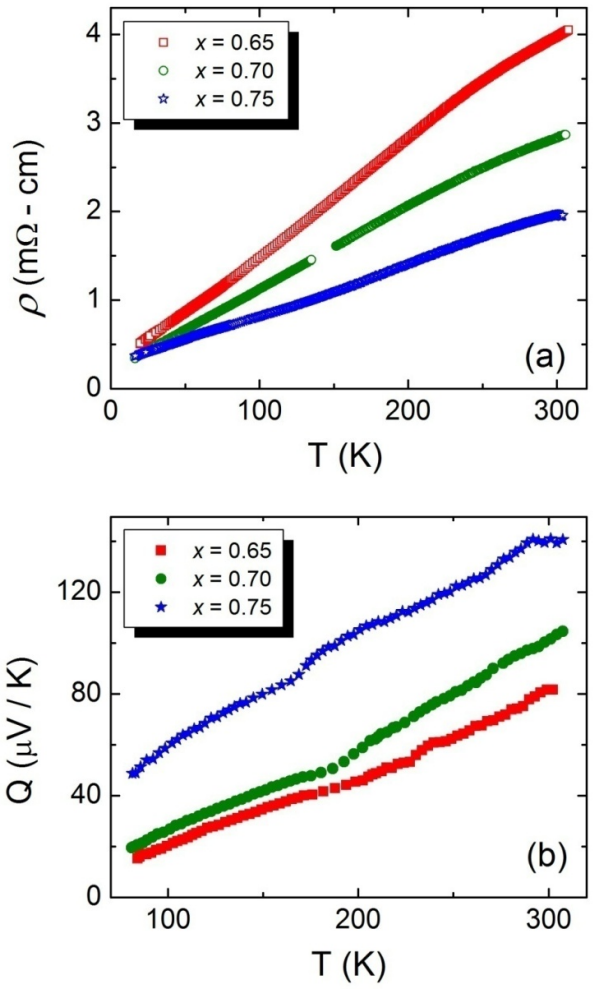

Figure. 2 – Temperature dependence of (a) electrical resistivity (ρ) and (b) thermoelectric power (Q) of Na_xCoO_2 with x = 0.65, 0.7 and 0.75.

In the present system, the two-dimensional metallic CoO_2 planes are electronically separated by the insulating layers of Na ions. The Co ions in each CoO_2 plane are arranged in a triangular lattice. This triangular geometry leads to speculation that the undoped compound (x = 0) with spin-1/2 Co^{4+} is a spin-frustrated Mott insulator. With increasing Na doping, charge carriers are introduced and the spin-1/2 Co^{4+} changes into spin-less Co^{3+} and as result resistivity decreases. The origin of the large value of Q in the metallic Na_xCoO_2 is yet to be understood. As Q and ρ depend on carrier density in similar ways, it is difficult to explain the large value of Q in metallic Na_xCoO_2 in terms of carrier density only. A possible way to explain the good metallicity is to take into account the role

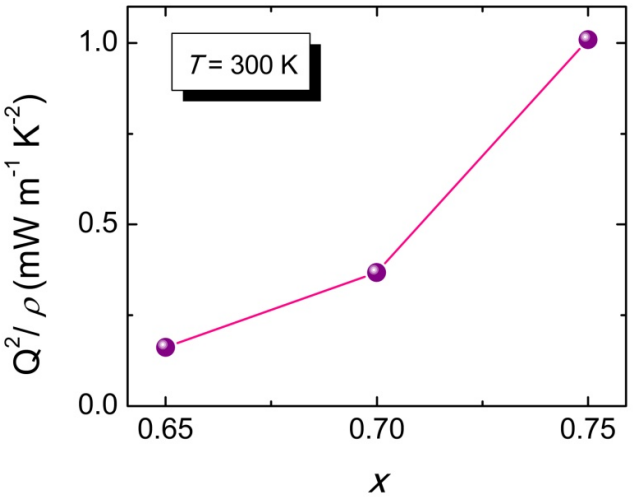

Figure. 3 - Power factor (Q^2/ρ) of Na_xCoO_2 as a function of x at 300 K.

of mobility of charge carrier because electrical conductivity is proportional to mobility but not the thermoelectric power.

CONCLUSIONS

In conclusion, we have investigated the temperature dependence of electrical resistivity, and thermoelectric power of Na_xCoO_2 with x = 0.65 – 0.75. For all samples, both resistivity and thermoelectric power increase with temperature. With increasing Na concentration, resistivity decreases whereas thermoelectric power increases. We have also calculated the power factor at 300 K for different x and observe that power factor increases very rapidly with Na concentration. For x = 0.75, the value of power factor becomes more than 1 $mWm^{-1}K^{-2}$, suggesting that Na_xCoO_2 could be a very promising material for use in high-temperature thermoelectric power generation devices.

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