Effect of Doping Radio on Thermoelectric Properties of Na$_{1-x}$Ag$_x$CO$_2$O$_4$

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Abstract. Oxide thermoelectric materials have the characteristics of simple conversion device structure and no environmental pollution. In this paper, a series of Na$_{1-x}$Ag$_x$CO$_2$O$_4$ thermoelectric materials with different doping radios were prepared by sol-gel synthesis method and microwave sintering method. Through the analysis of XRD, Seebeck coefficient, thermal conductivity and conductivity, the best effect is the doping ratio 0.3. To certain extent, the ZT value of the material is increased, and the relationship between nano scale and thermoelectric performance is obtained, which provides a new method for the preparation of thermoelectric materials.

Keywords. Thermoelectric materials, Na$_{1-x}$Ag$_x$CO$_2$O$_4$, thermoelectric properties, oxides, XRD.

NaCO$_2$O$_4$[1-2] is an oxide thermoelectric material with octahedral gap and layered. Study found that element doping or substitution can effectively enhance phonon scattering and induce lattice distortion, thereby improve the thermoelectric merit of the material. For example, Yakebe [3] et al. found that adding Ag can effectively improve the thermoelectric properties of NaCO$_2$O$_4$. Erdal et al. [4-5], found that NaCO$_2$O$_4$ can decompose and volatilize Na ions with the increase of temperature. In this paper, the influence of doping radio on the thermoelectric properties of Na$_{0.7}$Ag$_{0.3}$CO$_2$O$_4$ thermoelectric materials is studied on the basis of predecessors, which provides support for the possibility of improving the thermoelectric properties by doping control nano scale, and lays the experimental and theoretical foundation for the development of nano thermoelectric devices.

1. Experimental Scheme

NaNO$_3$, CO(NO$_3$)$_2$, 6H$_2$O, citric acid and AgNO$_3$ were used as raw materials to prepare powders by sol-gel method, then the granularity was changed by ball milling reaction synthesis method, and cold pressing was used to form a sheet with a diameter of 10 mm and a thickness of 2 mm, finally, the ceramic slices were prepared by microwave sintering.

X-Ray Diffractometer (Dandong square DX-2700) was used to precisely analyze the crystal structure of the samples, and the Seebeck Coefficient and resistivity were measured by using the Seebeck Coefficient and resistivity analysis system (lsr-3800, Linsay, Germany). The thermal conductivity was measured with a laser thermal conductivity analyzer (Germany LFA457). To ensure the accuracy of the results, all characterization tests were performed using the same sample.
2. Experimental Results and Analysis

Figure 1 is an XRD pattern with different doping radio. The characteristic diffraction peaks of NaCO$_2$O$_4$ and Ag are found in all samples by comparing with the standard card. With the increase of doping radio, the grain size first increases then decreases. According to the related literature, Ag is not a simple substitution in the doping process, but filled in the gap of lamellar structure, and the increase of holes results in the decrease of grain size.

![Figure 1. XRD pattern of Na$_{1-x}$Ag$_x$Co$_2$O$_4$ samples with different doping radio.](image)

With the increase of Ag content, the Ag particles filled in the larger gap can improve the conductivity of the material, and the larger specific surface area of Ag ions is beneficial to reduce the thermal conductivity of the material at the same time.

![Figure 2. The relationship between Seebeck Coefficient and temperature of Na$_{1-x}$Ag$_x$Co$_2$O$_4$ samples with different doping radio.](image)

Figure 2 shows the temperature dependence of Seebeck coefficients for samples with different doping radios. The Seebeck coefficients for all samples are positive, shows that the doping of Ag does not change the types of most carriers and the materials are still dominated by holes. The sample is P-type thermoelectric material. It can be seen from the diagram that the Seebeck Coefficient increases significantly with the increase of the temperature in the range of the rectification measurement, but with the increase of the Ag content, the change of the Seebeck Coefficient is more complicated, and the seebeck coefficient of Ag doped $x = 0.3$ sample is higher than that of other between 750 °C and 1100 °C, which means that the Seebeck Coefficient of Ag doped materials can increased in a certain range, and exceeding it will be disadvantageous to the increase of Seebeck coefficient. However, due to the strong correlation of narrow-band electrons, the relaxation time on Fermi surfaces decreases and the Seebeck Coefficient increases.
The surface doping may lead to the change of the carrier density, and the change of the carrier density will lead to the change of the resistivity and thermal conductivity. Figures 3 and 4 are the curves of the change of thermal conductivity and resistivity of samples with different doping ratio with temperature.

Since thermal conductivity is a function of thermal diffusivity, specific heat capacity at constant pressure and density, the relationship between thermal conductivity and temperature can be obtained by measuring thermal diffusivity, specific heat capacity at constant pressure and density. Figure 3 shows that the thermal conductivity increases with the increase of temperature. Comparing the thermal conductivity of samples with different doping ratios, it is found that the thermal conductivity of samples with doping radio of 0.3 first increases then decreases, which may be due to the disordered arrangement of Na itself. Therefore, the mass and radius of Ag Atom are very different from that of Na, so the thermal conductivity increases at first, but with the increase of Ag, the Phonon Free Path decreases, and the thermal conductivity decreases. At the same time, from the diagram that the thermal conductivity of the sample has little change with temperature and doping radio, because the thermal diffusivity and specific heat capacity at constant pressure of different samples are nearly equal in the course of testing, so the thermal conductivity of the sample has little difference.

Figure 3. Relationship between thermal conductivity and temperature of Na1-xAgxCo2O4 sample sintered at 800 °C.

Figure 4 show that doping will reduce the resistivity of the material because the resistivity of the material is composed of the internal grain resistance and the grain boundary resistance. According to the research of Yakabe [6], the grain boundary resistance plays a very small role, less than 1% Na ions will leave the original electron layer, thus creating electron hole and increasing the concentration of
carriers, which leads to the increase of the conductivity of the material, the resistivity of the material is reduced, the resistivity of the material is reduced after doping. Comprehensive analysis of the conductivity and resistivity of different doping radio shows that the effect is best when the doping radio is 0.3.

Figure 5 shows the variation of ZT value with temperature. Because ZT value is a comprehensive function of temperature, Seebeck, thermal conductivity and resistivity, the variation of ZT value with temperature is complicated under different doping radio, the doping radio of 0.3 is the ZT value, which indicates that this doping radio is suitable to improve the thermoelectric effect of the material.

![Figure 5](image)

Figure 5. Relationship between ZT value and temperature of Na1-xAgxCo2O4 sample sintered at 800 °C.

The results of XRD, SEM and thermoelectric properties show that nano-structure can induce quantum confinement effect, increase electronic density of states, and decouple the correlation between thermoelectric properties. Dresselhaus et al. theoretically demonstrated that the electronic density of states will split and narrow when the size is reduced to the nanometer scale, showing quantum confinement effect and effectively increasing the power of materials. In this study, the use of Ag doping increases the Na vacancy disorder. The thermoelectric properties are improved obviously, and this argument is fully verified.

Ag is attached to the lamellar structure so as not to affect its vacancy in the process of Ag doping, and the scattering of medium frequency phonons is increased in the nano-scale structure, and the free path range of low frequency phonons is covered by the grain boundary and other interfaces. The thermal conductivity of the material system is reduced by maximizing the multi-scale, the carrier concentration is increased by doping Ag at atomic scale, the Fermi energy level and the conduction band base are separated, the bipolar effect is suppressed, and the thermoelectric coefficient is increased.

In the whole phase transition process, the change of atomic occupancy configuration will increase the probability of phonon scattering and decrease the thermal conductivity. At the same time, the change of atomic occupancy will cause the change of electronic structure and effectively decouple the mutual restraint of various thermoelectric properties. And then regulate the behavior of thermoelectric transport.

3. Conclusion
(1) With the increase of doping amount, the particle size first increases then decreases;
(2) Seebeck Coefficient and thermal conductivity increase with temperature, and resistivity decrease with temperature;
(3) Ag doping increases Na vacancy disorder and can improve thermoelectric properties significantly. The best performance is obtained when the doping radio is 0.3.
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References
[1] Chen X 2011 Electronic structures and thermoelectric properties of NaCo$_2$O$_4$ thermoelectric material *Advanced Materials Research* **317-319** 2051-2054
[2] Demchenko D 2014 Lattice thermal conductivity in bulk and nanosheet Na$_x$CoO$_2$ *Physics Publications* **82** (1) 219-225
[3] Kurosaki K, Muta H, Uno M, et al. 2001 Thermoelectric properties of NaCo$_2$O$_4$ *Journal of Alloys and Compounds* **315** (1) 234-236
[4] Erdal M O, Koyuncu M, Uslu B 2014 The effect of synthesis technique on thermoelectric properties of nanocrystalline NaCo$_2$O$_4$ ceramics *Journal of Nanoparticle Research* **16** (2175) 1-8
[5] Ma F, Ou Y, Yang Y, et al. 2010 Nano crystalline structure and thermoelectric properties of electrospun NaCo$_2$O$_4$ nanofibers *J Phys. Chem. C* **114** 22038-22043
[6] Lis A, Park M S, Arroyave R, et al. 2014 Early stage growth characteristics of Ag$_3$Sn intermetallic compounds during solid-solid and solid-liquid reactions in the Ag-Sn interlayer system: Experiments and simulations *Journal of Alloys and Compounds* **617** (12) 763-773