

Effect of Preparation Process on Thermoelectric Performance of NaCo_2O_4

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Effect of preparation process on the thermoelectric properties of NaCo_2O_4 , which is so far the most promising oxide candidate for thermoelectric materials, was investigated. While calcining-calcining-sintering with adding 10% excess Na_2CO_3 at each step has been successful to obtain single phase samples, double-step sintering without addition of excess Na_2CO_3 turned out in this study to improve the thermoelectric properties. The doubly sintered sample showed increase in the Seebeck coefficient and the electrical conductivity, and thereby attained the power factor of $10 \times 10^{-4} \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-2}$ at 780°C . A very low thermal conductivity ($<1 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, at 800°C) resulted in $Z=1 \times 10^{-3} \text{ K}^{-1}$ and $ZT=1$ at a conservative estimate.

Key words: Seebeck coefficient, electrical conductivity, NaCo_2O_4 , preparation process

1. INTRODUCTION

NaCo_2O_4 consists of Na cations and CoO_2 blocks alternately stacking along the *c*-axis to form a layered structure [1]. Although the carrier mobility is ten times smaller than that of Bi_2Te_3 , which is one of the representative thermoelectric materials, the layered oxide NaCo_2O_4 shows large thermoelectric power and low electrical resistivity, and thus attains the power factor comparable to that of Bi_2Te_3 [2].

Although high operation temperatures lead to high thermoelectric conversion efficiency, most of thermoelectric materials being studied are unstable at high temperatures. However, oxides can be a promising materials to be used in the high temperature region [3,4,5]. Among several oxide candidates, the p-type thermoelectric performance of NaCo_2O_4 is outstanding [2,6,7]. Nevertheless, the reported data have been rather scattered, implying a strong dependence on preparation conditions.

In this paper, we have hence investigated the effect of preparation process on the thermoelectric properties of NaCo_2O_4 .

2. EXPERIMENTAL

Sintered samples of NaCo_2O_4 were prepared by solid state reaction from fine powders of Co_3O_4 (>99.95%) and Na_2CO_3 (>99.5%) as shown in Fig. 1. The mixed powder was calcined twice at 800°C and sintered at 900°C with adding 10% excess Na_2CO_3 at each heating process (single-step sintering). We have further examined double-step sintering, in which the sintered body was pulverized and sintered again without adding excess Na_2CO_3 (see Fig. 1). A powder X-ray diffraction study was carried out to identify crystal phases. Specimens for the electrical

measurements were cut out from the sintered bodies into a rectangular shape of about $3 \times 6 \times 13 \text{ mm}^3$ in size. The electrical conductivity was measured by 4-wire method. The thermoelectric power (Seebeck coefficient) was determined from the slope of the least-squares regression of ΔV vs. ΔT plotting, where ΔV is voltage generated between both ends of specimen, across which various temperature difference ΔT (about $2 \text{ K} \sim 10 \text{ K}$) being applied. Scanning electron microscopic (SEM) observation was carried out on fracture surfaces of the sintered samples in order to examine anisotropic crystal growth.

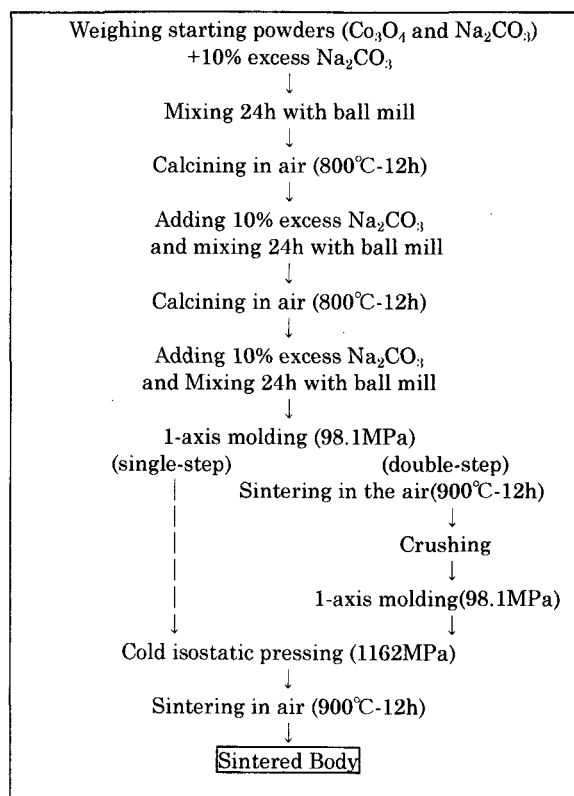
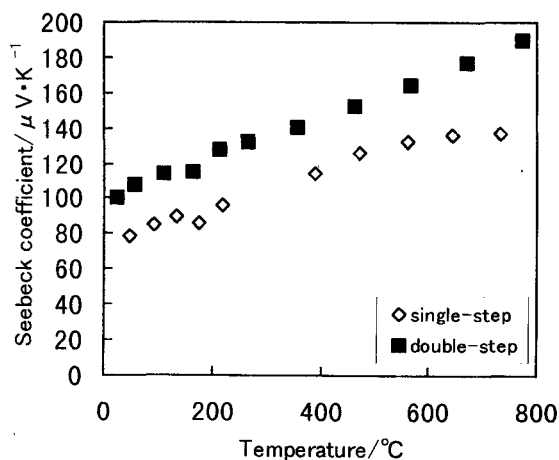
3. RESULTS AND DISCUSSION

The temperature dependence of the Seebeck coefficient (*S*) for the samples prepared by single-step and double-step sintering is shown in Fig. 2. In both cases *S* increased with increasing temperature. However, *S* for the sample sintered in double-step is 20% to 30% larger than that for the single-step sintering, and reaches about $200 \mu\text{V/K}$ at 780°C .

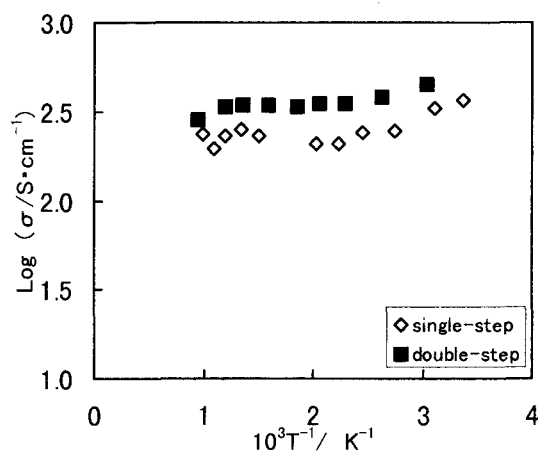
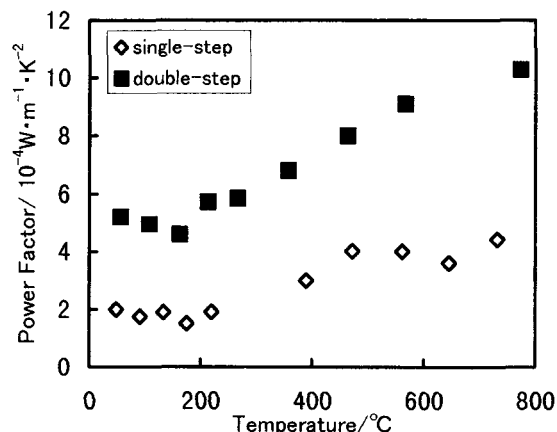
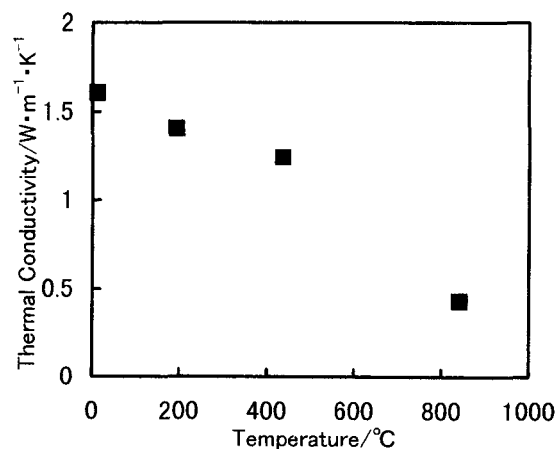
The temperature dependence of the electrical conductivity (σ) of the samples is shown in Fig. 3. In both cases σ decreased with temperature, showing metallic conduction with the values around $300 \text{ S} \cdot \text{cm}^{-1}$. Noteworthy, σ moderately increased by double-step sintering, while *S* also increased.

Fig. 4 shows that the power factor values are more than twice for the double-step sintering. The power factor increased with temperature and reached $10 \times 10^{-4} \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-2}$.

The thermal conductivity, κ , for double-step sintered body is shown in Fig. 5. The κ value was as low as $1.6 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at room temperature, and further decreased with increasing temperature down to $0.5 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at 850°C . Although the data were averaged over three measured

Fig. 1 The preparation processes of NaCo_2O_4 .Fig. 2 The temperature dependence of the Seebeck coefficient of NaCo_2O_4 prepared by single- and double-step sintering.

values at one data point and the deviation between each measurement was very small ($<2\%$), one might consider the κ value of $0.5 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ is too low. Nevertheless, development of the layered structure associated with anisotropic crystal growth (see below) might be a reason of these very low κ values. Even assuming κ conservatively as $1 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at 780°C , we could obtain $Z=1.0 \times 10^{-3} \text{ K}^{-1}$ and thereby $ZT=1.0$ (if we take straight the measured value, we would obtain $Z=2 \times 10^{-3} \text{ K}^{-1}$ and $ZT=2$).

Fig. 3 The temperature dependence of the electrical conductivity of NaCo_2O_4 .Fig. 4 The temperature dependence of the power factor of NaCo_2O_4 .Fig. 5 Thermal conductivity for double-step sintered NaCo_2O_4 .

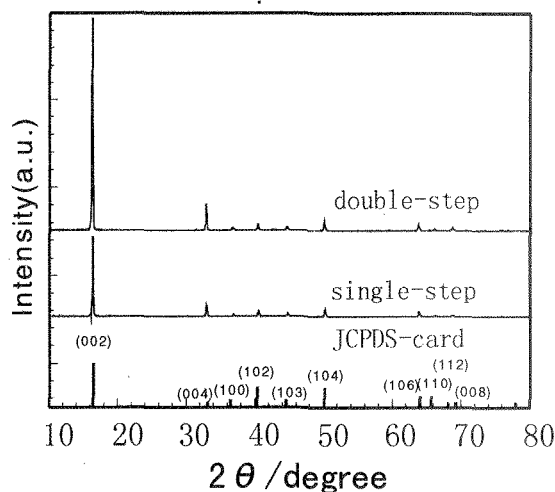


Fig. 6 The XRD patterns of sintered NaCo_2O_4 .

Fig. 6 shows a comparison of the XRD patterns of the samples and that in the literature [8]. The most noticeable feature is that the intensity of the (00l) ($l=2,4,8$) peaks is stronger than that of, e.g. (100) and (102), for the sintered samples compared to the JCPDS data. These results imply strongly anisotropic crystal growth perpendicular to the c -axis, which may also cause a preferential orientation of the crystallites.

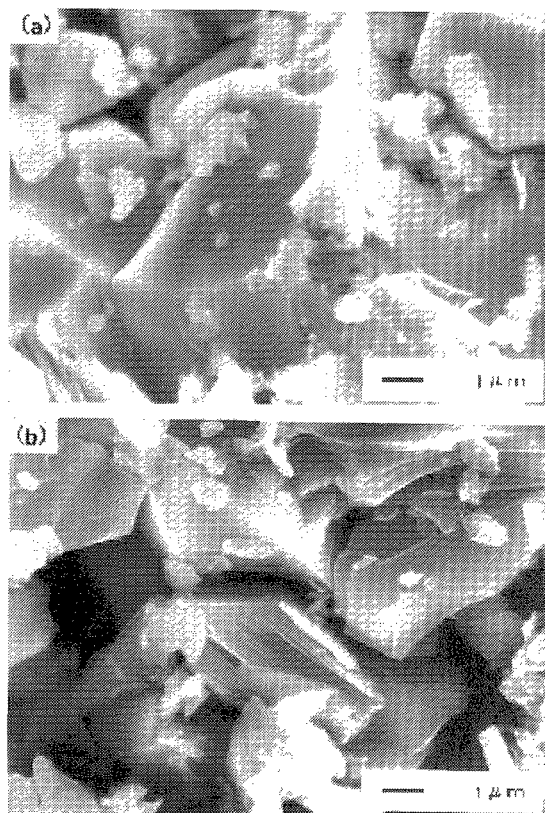


Fig. 7 SEM images of fracture surfaces of sintered NaCo_2O_4 .
(1) single-step sintered sample
(2) double-step sintered sample

Moreover, the intensity ratio of $I(002)/I(102)$ is much larger for double-step sintering than that for single-step sintering, suggesting a further development in the two-dimensionality.

We have hence further examined microstructure of the sintered samples by the SEM observation. Fig. 7 compares the fracture surfaces of the samples prepared by single- and double-step sintering. The size of large crystallites appears to be almost the same and isotropic for both samples, showing no noticeable preferential crystal orientation even for the double-step sintering. However, platelike crystallites also exists in Fig. 7(b), and a well developed layered structure showing cleavage planes between the layers is clearly observed on the crystallites in Fig. 7(b), contrasting to smooth and structureless surface seen in Fig. 7(a). Whereas no preferential orientation of the crystallites caused by anisotropic crystal growth was verified, these results demonstrate for the sample prepared by double-step sintering a considerable development in the two-dimensionality (perpendicular to the c -axis) within the crystallites, which would lead to a significant decrease in the crystal defects and disorders. Since no preferential orientation was observed in the microstructure of the samples, the improvement in the thermoelectric properties by the double-step sintering may probably be isotropic.

Because the data reported on a NaCo_2O_4 single crystal have implied much higher performance [2] (power factor $= 50 \times 10^{-4} \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-2}$ and estimated $Z = 3.3 \times 10^{-3} \text{ K}^{-1}$ at 300K) than those ever reported on sintered samples, approaching to a more single crystal-like structure may account for the significant improvement in the thermoelectric properties by double-step sintering.

4. CONCLUSIONS

The effect of preparation process on the thermoelectric properties of NaCo_2O_4 was investigated. The sample prepared by solid state reaction with double-step sintering showed better thermoelectric properties than single-step sintering, and consequently the power factor reached $10 \times 10^{-4} \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-2}$ at 780°C . The κ value was lower than $1 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at high temperature, and thus the sample attained the figure of merit $Z = 1 \times 10^{-3} \text{ K}^{-1}$ and $ZT = 1.0$ at 780°C at a conservative estimate. These values are obviously highest among the oxide candidate materials, and are the best results ever reported on sintered NaCo_2O_4 .

The sintered samples showed strongly anisotropic XRD patterns. It was suggested that the development in the two-dimensional layered structure within the crystallites would be responsible for the highly improved thermoelectric performance.

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