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Thermoelectric properties of Li-doped $Cu_{0.95-x}M_{0.05}Li_xO$ (M=Mn, Ni, Zn)

N. Yoshida, T. Naito and H. Fujishiro*
(* corresponding author: fujishiro@iwate-u.ac.jp)
Faculty of Engineering, Iwate University, 4-3-5 Ueda, Morioka 020-8551, Japan.

ABSTRACT

Thermoelectric properties of the Li-doped $Cu_{0.95-x}M_{0.05}Li_xO$ (M=divalent metal ion; Mn, Ni, Zn) were investigated at the temperature up to 1273 K. In the doped divalent metal ions, Zn^{2+} ion was the most effective to reduce the thermal conductivity, and the Ni^{2+} substitution was preferable to decrease the electrical resistivity. For the $Cu_{0.95-x}Ni_{0.05}Li_xO$ sample at x=0.03, the maxima of the dimensionless thermoelectric figure of merit ZT and the power factor P at 1246 K were 4.2×10^{-2} and 1.6×10^{-4} W/K^{2}m, respectively. The enhancement of the thermoelectric properties of the Li-doped $Cu_{0.95-x}M_{0.05}Li_xO$ system was discussed.

INTRODUCTION

The thermoelectric technology using a waste heat for electric power generation devices has been revised because of recent energy crisis besides other renewable energy sources. Since the discovery of $NaCo_2O_4$ in 1998 [1], oxide thermoelectric materials have been intensively studied using Ca-Co-O and $NaCo_2O_4$ systems with layered Co-O octahedron [2,3], as a substitute for the conventional semiconductors such as Bi_2Te_3. However, the thermoelectric performance has been still low. In material researches for thermoelectricity, we focus on the possibility of a conventional CuO system, because it is inexpensive, plentiful and non-toxic resources. CuO is known to be a metal deficient p-type semiconductor with a band gap of 1.2 eV with monoclinic crystal structure, and many studies were reported for the physical properties [4,5]. High-purity CuO has a large positive Seebeck coefficient S, but shows both a high electrical resistivity ρ and a high thermal conductivity κ. If the doping or substitution of univalent or trivalent ions is possible for the Cu site, the electrical resistivity and the thermal conductivity might be decreased. In this case, the thermoelectric efficiency may be enhanced, if the Seebeck coefficient is not deteriorated so much. Similarly to the CuO system, ZnO is a plentiful and promising material for the n-type thermoelectricity with a simple wurtzite structure [6]. The electrical resistivity ρ drastically decreases by the doping of a small amount of Al^{3+} and/or Ga^{3+}, and the dimensionless thermoelectric figure of merit ZT ($=S^2T/\rho\kappa$) reaches 0.3 and 0.65 at 1273 K for $Zn_{0.98}Al_{0.02}O$ and $Zn_{0.96}Al_{0.02}Ga_{0.02}O$, respectively [7,8]. For the CuO system, the electric conductivity σ ($=1/\rho$) and Seebeck coefficient S were reported for the Li and Al doping, in which the Li-doping enhances the p-type electrical conductivity [9]. However, a systematic investigation has not been performed as a thermoelectric material of CuO as for the doping species and the optimum doping concentration.

Recently, we have reported the alkali metal substitution for the Cu-site in CuO, in which Li^+ is the most promising ion to enhance the thermoelectric performance. The ZT takes a maximum of 3.2×10^{-2} at 1246 K for the $Cu_{0.97}Li_{0.03}O$ [10]. To enhance the thermoelectric performance, the reduction of the thermal conductivity is a possible approach, which is usually realized by the substitution of the element with different ionic radius.

In this study, we fabricated the Li-doped $Cu_{0.95-x}M_{0.05}Li_xO$ (M=Mn, Ni, Zn) and measured thermoelectric properties at high temperature. The potential of the CuO system as thermoelectric materials was discussed.

EXPERIMENT

$Cu_{0.95-x}M_{0.05}Li_xO$ polycrystals doped with a divalent-metal element (M=Mn, Ni, Zn) were prepared by a conventional solid-state reaction. The raw powders of CuO (Furuuchi Chemical; 99.9%), MnO (KOJUNDO; 99.9%), NiO (Furuuchi Chemical; 99.9%), ZnO (KOJUNDO; 99.9%) and Li_2O (KOJUNDO; 99% up) were mixed with a molar ratio of Cu:M:Li=0.95-x:0.05:x (x=0.01, 0.03). The specimen was pressed cold-isostatically under 64 MPa into a bar and then sintered at 1060℃ for 10 h in oxygen flow. The measured densities of each sample were greater than 95% of the ideal density. The rectangular-shaped specimen with about 2 x 2 x 10 mm^3 was cut from the bar for the measurements of the thermoelectricity. Powder X-ray diffraction measurements were performed at 300 K using a Cu $K\alpha$ radiation (Rigaku; Multi Flex) in the range of $20° \leqq 2\theta \leqq 90°$ with 0.02° steps. The electrical resistivity $\rho(T)$ and Seebeck coefficient $S(T)$ were simultaneously measured in the temperature range from 300 to 1273 K using an automated measuring system (Ozawa Science; RZ2001i) and the thermoelectric power factor $P=S^2/\rho$ was calculated. Low-temperature thermal conductivity $\kappa(T)$ was measured by a steady-state heat flow method from 10 to 300 K using a home-made apparatus combined with helium refrigerator [11]. High-temperature thermal conductivity $\kappa(T)$ was also measured by a laser flash method (Ulvac-Riko; TC-7000) up to 1023 K. $\kappa(T)$ was extrapolated up to 1300 K using a fitting curve which was proportional to T^{-1} for the experimental $\kappa(T)$ results at low and high temperatures. A dimensionless figure of merit $ZT=S^2T/\rho\kappa$ was estimated using these values.

DISCUSSION

Thermal conductivity of $Cu_{0.95}M_{0.05}O$ (M=Mn, Ni, Zn)

The doping effect of divalent metal (M) ion in CuO on the thermal conductivity $\kappa(T)$ was investigated. Figure 1 shows the temperature dependence of $\kappa(T)$ of pure CuO and $Cu_{0.95}M_{0.05}O$ (M=Mn, Ni, Zn). $\kappa(T)$ was reduced by the substitution for the Cu-site, in which the Zn substitution is the most effective. The $\kappa(T)$ reduction by the divalent metal ion doping seems to be the introduction of the lattice disorder due to the substitution of the M ion for the Cu site with difference of the ionic radius. $\kappa(T)$ of materials can be generally represented by the sum of lattice contribution (κ_{ph}) and carrier contribution (κ_e). In the present samples, heat propagates almost due to phonons (κ_{ph}) because of the high $\rho(T)$ value. The measured $\kappa(T)$ shows a broad peak at low temperature, which results from the phonon-phonon scattering as can be seen in insulating materials. In the previous paper, we reported that the thermoelectric properties were enhanced by the Li doping to the CuO matrix [10]. In the later subsection, we report on the Li doping effect on the thermoelectric properties of $Cu_{0.95}M_{0.05}O$ with smaller $\kappa(T)$.

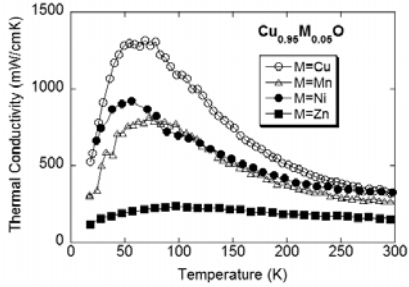

Figure 1. Temperature dependence of the thermal conductivity $\kappa(T)$ of pure CuO and $Cu_{0.95}M_{0.05}O$ (M=Mn, Ni, Zn).

Thermoelectric properties of Li-doped $Cu_{0.95-x}M_{0.05}Li_xO$ (M=Ni, Zn)

Figures 2(a) and 2(b) show the temperature dependence of the electrical resistivity $\rho(T)$ and Seebeck coefficient $S(T)$ for the Li-doped $Cu_{0.95-x}M_{0.05}Li_xO$ (M=Ni, Zn). In Fig. 2(a), $\rho(T)$ of the $Cu_{0.95}M_{0.05}O$ samples decreased with increasing T at T<800 K, compared with pure CuO, but was comparable with that of the pure CuO at higher temperatures. Similarly to the Li-doped CuO [10], the Li doping can drastically reduce the $\rho(T)$ and the absolute value of $\rho(T)$ decreased with increasing contents of Li. $\rho(T)$ of the $Cu_{0.95-x}Ni_{0.05}Li_xO$ is lower than that of the $Cu_{0.95-x}Zn_{0.05}Li_xO$ at identical x, both of which are lower than that of the Li-doped $Cu_{1-x}Li_xO$. In Fig. 2(b), $S(T)$ decreases with increasing x. $S(T)$ of the $Cu_{0.95-x}Ni_{0.05}Li_xO$ is lower than that of the $Cu_{0.95-x}Zn_{0.05}Li_xO$ at identical x, both of which are lower than that of the Li-doped $Cu_{1-x}Li_xO$ [10]. Because $S(T)$ is closely correlated with $\rho(T)$ [12].

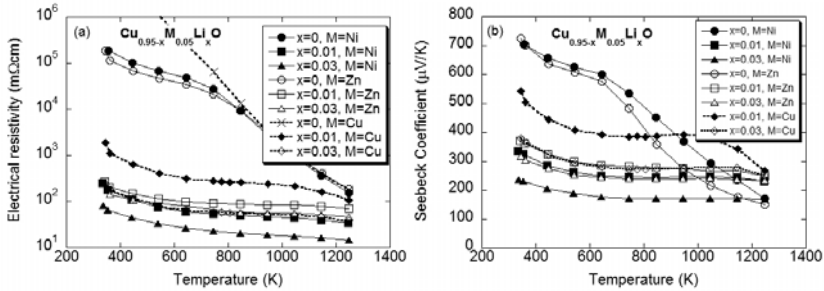

Figure 2. Temperature dependence of (a) the electrical resistivity $\rho(T)$ and (b) the Seebeck coefficient $S(T)$ of pure CuO and Li-doped $Cu_{0.95-x}M_{0.05}Li_xO$ (M=Ni, Zn).

Figure 3(a) shows the x dependence of the thermal conductivity $\kappa(T)$ of the Li-doped $Cu_{0.95-x}M_{0.05}Li_xO$ (M=Ni, Zn). As shown in Fig. 1, the $\kappa(T)$ reduction by the Zn substitution was larger than that by the Ni substitution, both of which $\kappa(T)$ further decreased with increasing

content of Li, x. The origin of the additional $\kappa(T)$ reduction by the Li doping comes from the introduction of the disorder in the lattice.

Figure 3(b) shows the $\kappa(T)$ of the $Cu_{0.94}Ni_{0.05}Li_{0.01}O$ sample up to 1000 K. The fitting curve, which was proportional to T^{-1}, was also shown and was extrapolated up to 1273 K. The estimated $\kappa(T)$ value was 52 mW/cmK at 1200 K, which was smaller than that for the $Cu_{0.99}Li_{0.01}O$ sample [10] due to the enhanced disorder by the additional Ni substitution.

Figure 4(a) depicts the temperature dependence of the thermoelectric power factor $P(T)$ of the Li-doped $Cu_{0.95-x}M_{0.05}Li_xO$ (M=Ni, Zn). $P(T)$ of the $Cu_{0.97}Li_{0.03}O$, which showed the highest $P(T)$ in the previous paper [10] is also shown. As would be expected from the results of $\rho(T)$ and $S(T)$ values, $Cu_{0.95-x}Ni_{0.05}Li_xO$ (x=0.03) shows the highest $P(T)$ of 2.0×10^{-4} W/K^{2}m at 1246 K, which is higher than that for $Cu_{0.97}Li_{0.03}O$.

Figure 4(b) shows the dimensionless figure of merit ZT of the Li-doped $Cu_{0.95-x}M_{0.05}Li_xO$ (M=Ni, Zn) as a function of T. The ZT value increased with increasing temperature and contents of Li, and took a maximum value of 4.2×10^{-2} for $Cu_{0.95-x}Ni_{0.05}Li_xO$ (x=0.03) at 1246 K, which was about 30% larger than that of $Cu_{0.97}Li_{0.03}O$. The enhancement of the ZT value was also confirmed for the $Cu_{0.95-x}Zn_{0.05}Li_xO$ system. The reduction of $\kappa(T)$ and $\rho(T)$ by the Ni or Zn substitution besides the Li doping enhances the thermoelectric properties.

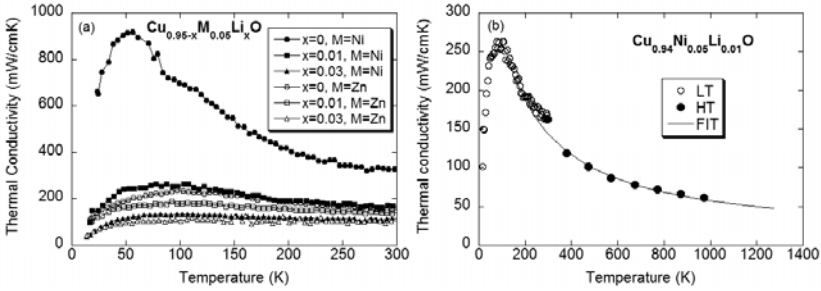

Figure 3. Temperature dependence of the thermal conductivity $\kappa(T)$ of $Cu_{0.95-x}M_{0.05}Li_xO$ (M=Ni, Zn) at $T\leq300$ K and (b) $\kappa(T)$ for $Cu_{0.94}Ni_{0.05}Li_{0.01}O$ up to 1000 K. The extrapolated fitting curve up to 1300 K is also shown.

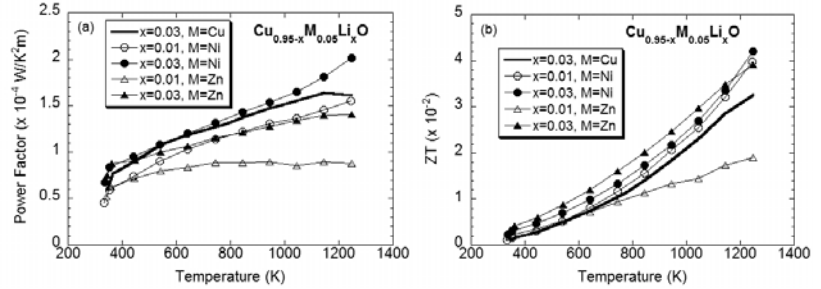

Figure 4. Temperature dependence of the (a) power factor P and (b) dimensionless figure of merit ZT of $Cu_{0.95-x}M_{0.05}Li_xO$ (M=Ni, Zn).

CONCLUSIONS

We have investigated the thermoelectric properties of the Li-doped $Cu_{0.95-x}M_{0.05}Li_xO$ (M=Mn, Ni, Zn) as thermoelectric materials. Important experimental results and conclusions obtained from this study are summarized as follows.

1) Among the divalent metal substitution for the Cu-site in $Cu_{0.95}M_{0.05}O$, Zn^{2+} is the most promising ions to decrease the thermal conductivity. The $\kappa(T)$ reduction seems to be the effect of the lattice disorder by the substitution of Zn for the Cu site.
2) For the $Cu_{0.95-x}M_{0.05}Li_xO$ (M=Ni, Zn), the electrical resistivity $\rho(T)$, Seebeck coefficient $S(T)$ and the thermal conductivity $\kappa(T)$ decreased with increasing contents of Li up to x=0.03. Power factor $P(T)=S^2/\rho$ increased with increasing contents of Li, takes a maximum of $P=2.0\times10^{-4}$ W/K^{2}m at 1246 K.
3) For the $Cu_{0.92}Ni_{0.05}Li_{0.03}O$, the dimensionless thermoelectric figure of merit $ZT=S^2T/\rho\kappa$ increased with increasing contents of Li. A maximum of $ZT=4.2\times10^{-2}$ was realized at 1246 K which was about 30% larger than that of $Cu_{0.97}Li_{0.03}O$.

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