Thermoelectric Properties of Li-Doped CuO

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Thermoelectric Properties of Li-Doped CuO

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Thermoelectric properties of CuO doped with alkali metal ions (Li⁺, Na⁺, K⁺) were investigated at temperatures up to 1273 K. Among the doped alkali metal ions, Li⁺ ion was the most effective to enhance the thermoelectric properties. The maximum dimensionless thermoelectric figure of merit ZT and power factor P were, respectively, 3.2 × 10⁻² and 1.6 × 10⁻⁴ WK⁻²m⁻¹ at 1246 K for the 3.0%-Li-doped CuO. The enhancement of the thermoelectric properties of the CuO system was discussed.

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1. Introduction

The thermoelectric technology of using waste heat for power generation devices has been revived because of the recent energy crisis along with other renewable energy sources. Since the discovery of NaCoO₂ in 1997,¹ oxide thermoelectric materials have been intensively studied using Ca–Co–O and NaCoO₂ systems²⁻⁵ with layered Co–O octahedra, as a substitute for conventional semiconductors such as Bi₂Te₃. However, the thermoelectric performance is low. In material research for thermoelectricity, we focus on the possibility of a conventional CuO, because it is inexpensive, plentiful and nontoxic. CuO is known to be a metal-deficient p-type semiconductor with a band gap of 1.2 eV and a monoclinic crystal structure, and many studies have been reported on its physical properties.⁶⁻¹¹ 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 S is not greatly deteriorated. Similar to CuO, ZnO is plentiful and has a simple wurtzite structure, making it a promising material for n-type thermoelectricity.¹² The electrical resistivity drastically decreases upon doping of a small amount of Al³⁺ and Ga³⁺, and the non-dimensional thermoelectric figure of merit ZT (≡ S²T/ρκ) reaches 0.3 and 0.65 at 1273 K for Zn₀.₉₈Al₀.₀₂O and Zn₀.₉₆Al₀.₀₂Ga₀.₀₂O, respectively.¹³¹⁴ For the CuO system, the electric conductivity σ (≡ 1/ρ) and Seebeck coefficient S have been reported for Li⁺ and Al-doped CuO,¹⁵ in which the Li-doping enhances the p-type electrical conductivity. However, a systematic investigation has not been performed as a thermoelectric material with respect to the doping species and their optimum concentrations.

In this study, we investigated the CuO polycrystals doped with alkali metals (Li, Na, K) and measured the electrical and thermal properties. The potential of CuO as a thermoelectric material was discussed.

2. Experimental Procedure

CuO polycrystals doped with an alkali-metal element (Li, Na, K) were prepared by a conventional solid-state reaction. For Li-doping, CuO (Furuuchi Chemical or DOWA Mining, 99.9%) and Li₂CO₃ (Furuuchi Chemical, 99.9%) were mixed with a molar ratio of Cu : Li = 1−x : x (0 ≤ x ≤ 0.07) and were calcined at 760°C for 12 h in air. In this study, we abbreviate the Li-doped CuO as (Cu₁−xLiₓ)O. For Na- and K-doping, only x = 0.01 samples were prepared, using Na₂CO₃ (Furuuchi Chemical, 99.9%) and K₂CO₃ (Furuuchi Chemical, 99.9%) as raw materials. The precursors were re-ground, pressed cold-isostatically under 64 MPa into a bar and then sintered at 1060°C for 10 h in oxygen flow. The measured densities of each sample were greater than 95% of the ideal density. A rectangular specimen of about 2 × 2 × 7 mm³ was cut from the bar for the measurements of thermoelectricity. Powder X-ray diffraction measurements were performed at 300 K using Cu Kα radiation (Rigaku Multi Flex) in the range of 2θ = 20° ≤ 2θ ≤ 90° with 0.02° steps, and lattice parameters were determined using a Rietveld profile refinement program, RIETAN 2000.¹⁶ The electrical resistivity ρ(T) [or electrical conductivity σ(T) = 1/ρ(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 = S²/ρ was calculated. Low-temperature thermal conductivity κ(T) was measured by a steady-state heat flow method from 10 to 300 K using a home-made apparatus combined with a helium refrigerator.¹⁷¹⁸ High-temperature thermal conductivity κ(T) was also measured by a laser flash method (Ulvac-Riko TC-7000) up to 1023 K. κ(T) was extrapolated up to 1300 K using a fitting curve for the relationship with T⁻¹ for the experimental κ(T) results at low and high temperatures. A dimensionless figure of merit ZT = S²T/ρκ was estimated using these values.

3. Results and Discussion

3.1 Doping effect of alkali metal in CuO on thermoelectricity

The doping effect of alkali metals in CuO on the electrical conductivity σ(T) = 1/ρ(T) and Seebeck coefficient S(T) was investigated. Figure 1(a) shows the temperature dependence of σ(T) of pure (nondoped) CuO and 1.0% alkali-metal (M = Li, Na, K)-doped Cu₀.₹₉M₀.₀₁O. σ(T) among all the samples show a semiconducting behavior and increase with increasing temperature. The plot of the log σ vs 1/T curve is linear with a bending point at T*. The activation energy at low temperature (T < T*) is lower than that at high temperature (T > T*). T* of the nondoped CuO is about 720 K. It increases with increasing σ(T) for the doped CuO. Li-doped CuO shows the highest σ(T), which is about four orders of magnitude larger than that for the pure CuO.
at 400 K. Although the ionic radii of Li$^+$ (0.76 Å), Na$^+$ (1.02 Å), and K$^+$ (1.38 Å) increase with increasing atomic number, $\sigma(T)$ of Cu$_{0.99}$M$_{0.01}$O decreases for M = Li, K, and Na in this order. Li$^+$ is of a comparable size to Cu$^{2+}$ (0.73 Å) and may be preferable for occupying the vacancy site of Cu or to replace the Cu$^{2+}$ site; then the effective hole carriers will be introduced because of ionic size matching. Another possible explanation of the order of $\sigma(T)$ for Cu$_{0.99}$M$_{0.01}$O is the difference in the solubility of the alkaline atoms in CuO; the solubility of Li may be the highest and that of Na may be the lowest, although no impurity phases can be confirmed for the Cu$_{0.99}$Na$_{0.01}$O sample from the XRD results.

Figure 1(b) shows the temperature dependence of $S(T)$ of 1.0%-alkali-metal (M = Li, Na, K)-doped Cu$_{0.99}$M$_{0.01}$O. The sign of $S(T)$ shows p-type semiconducting properties throughout the entire temperature range. The absolute value of $\sigma(T)$ reflects that of $S(T)$; the lower the $\sigma(T)$ value becomes, the higher $S(T)$ reaches, as predicted by the conventional theory. The inflection temperature of $S(T)$ corresponds to the bending point $T^*$ in $\sigma(T)$ for the doped samples. In Fig. 1(b), it should be noted that $S(T)$ of nondoped CuO is apparently quite strange; it is a large positive value around room temperature and changes its sign at 600 K, becoming negative large values, and then recovers to positive values at higher temperatures. The type-change behavior of $S(T)$ was reversibly and reproducibly observed for the nondoped CuO fabricated under the present conditions. No anomalous $S(T)$ behavior can be observed, and $S(T)$ is positive over the entire temperature range for the nondoped CuO, which was sintered at a lower temperature than 1050 °C using the same raw powder. The re-entrant $S(T)$ behavior is closely related to the defect/impurity chemistry of CuO. A negative conducting channel such as Cu$^+$ may exist, and the compensating effect occurs at low and high temperatures. The mechanism of the type change is not yet understood and a detailed study using the results of the Hall effect is in progress.

Figure 2 shows the temperature dependence of the power factor $P = S^2\sigma$. $P(T)$ for the doped-samples increases with increasing $T$. Li-doped Cu$_{0.99}$Li$_{0.01}$O shows the highest $P$ value of 7.45 × 10$^{-5}$ W K$^{-2}$ m$^{-1}$ at 1250 K, which results from the large $\sigma$ value in spite of the $S$ value being the smallest. In the following subsection, we focus on the thermoelectric properties of Li-doped CuO and investigate the relationship between the contents of doped Li and the thermoelectric properties.

### 3.2 Thermoelectric properties of Li-doped CuO

X-ray diffraction measurement was performed in order to confirm the effect of Li-doping on the lattice parameters. Figure 3 presents the lattice parameters as a function of the Li content. The crystal structure of the Li-doped CuO was confirmed to be monoclinic at 300 K without an impurity peak until $x = 0.04$. The lattice parameter $a$ seemed to increase slightly, the lattice parameters $b$ and $c$ decreased with increasing Li content. The angle $\beta$ also increased monotonically with doping. As a result, the unit-cell volume $V_{\text{cell}}$ decreased with doping and $V_{\text{cell}}$ of the $x = 0.04$ sample was 0.11% smaller than that of the nondoped CuO. These results suggest that Li substituted into the Cu site or occupied the vacancy site of Cu up to $x = 0.04$. The obtained lattice parameters $a$ and $c$ were scattered slightly for the $x = 0.02$ sample, which may result from the finite deviation between experimental and theoretical XRD patterns.

Figure 4(a) depicts the temperature dependence of the electrical resistivity $\rho(T)$ for Li-doped (Cu$_{1-x}$Li$_x$)O (0.0005 $\leq x \leq 0.05$), (Cu$_{1-x}$Li$_x$)O with $x = 0.0005$ and 0.001 shows semiconducting behavior, which indicates the activation type. For the samples with 0.005 $\leq x \leq 0.05$, $\rho(T)$ drastically decreases with increasing $x$, is minimum at $x = 0.03$, and then increases slightly with an increase in $x$. For the Cu-site substitution by a Li$^+$ ion, a hole is produced.

Fig. 1. (Color online) Temperature dependence of (a) electrical conductivity $\sigma(T)$ and (b) Seebeck coefficient $S(T)$ of pure (nondoped) and 1.0% alkali-metal (Li, Na, K)-doped CuO. The arrows show the inflection temperature $T^*$ (see text).

Fig. 2. (Color online) Temperature dependence of power factor $P = S^2\sigma$ of 1.0% alkali-metal (Li, Na, K)-doped CuO.

Li-doped CuO and investigate the relationship between the contents of doped Li and the thermoelectric properties.
The absolute value and temperature dependence of the Seebeck coefficient, the Hall effect must be performed. The slight increase in \( \rho(T) \) for \( x \geq 0.04 \) may come from the introduction of the lattice disorder or solubility limit of Li in CuO. Figure 4(b) shows the \( \rho \) value at 745 and 1145 K, as a function of the contents of Li. In the figure, the dashed line shows the linear relation \( \rho \propto 1/x \). Roughly speaking, the \( \rho \) value is inversely proportional to the nominal carrier concentration \( x \). In a simple relation, \( \rho \) can be represented as \( \rho \propto 1/e\kappa_p\mu_p \), where \( e \) is the charge of an electron, \( \kappa_p \) the effective carrier concentration, and \( \mu_p \) the mobility of the hole carrier. In order to clarify the \( \kappa_p \) and \( \mu_p \) values, the measurement of the temperature dependence of the Hall effect must be performed.

Figure 5(a) presents the temperature dependence of the Seebeck coefficient \( S(T) \) of Li-doped \((\text{Cu}_{1-x}\text{Li}_x)\text{O}\) with \( 0.0005 \leq x \leq 0.05 \). For \( x = 0.0005 \) and 0.001, \( S(T) \) is a positive high value at \( T \leq 700 \) K because of large \( \rho(T) \) and then sharply decreases with increasing \( T \). For \( x \geq 0.005 \), the \( S(T) \) value decreases with decreasing \( x \) until \( x = 0.03 \) as \( \rho(T) \) decreases, but slightly increases with increasing \( x \). The absolute value and temperature dependence of \( S(T) \) are closely correlated with \( \rho(T) \). Figure 5(b) shows the theoretical estimation of \( S \) at \( T = 773 \) K using the Heikes formula \( S = (k_B/e) \ln((1 - x)/x) \), where \( k_B \) is the Boltzmann constant. The results suggest that the theoretical \( S \) value reproduces the measured one qualitatively, which is also reproduced at 500–1000 K.

Figure 6(a) shows the temperature dependence of the thermal conductivity \( \kappa(T) \) of Li-doped CuO at \( T \leq 300 \) K. \( \kappa(T) \) of all the samples shows a broad peak at 60 K, which results from phonon–phonon scattering, as well seen in insulating materials. \( \kappa(T) \) decreases with increasing \( x \) up to \( x = 0.03 \) and then slightly increases with an increase in \( x \). \( \kappa(T) \) of the \( x = 0.03 \) sample is one-third that of the nondoped sample, which is a desirable situation for thermoelectricity. The \( \kappa(T) \) reduction upon the Li-doping seems to be the effect of the lattice disorder due to the substitution of Li into the Cu site. Since the electronic thermal conductivity \( \kappa_e \) was estimated using the Wiedemann–Franz law, was negligibly small, the heat transport was performed entirely by phonons. Figure 6(b) shows \( \kappa(T) \) of the typical samples at high temperature, as measured by a laser flash method. The fitting curves, which are proportional to \( T^{-1} \), are also shown, extrapolated up to 1273 K. The \( \kappa \) values at 1200 K were estimated to be about 60 mW/cm K, independent of the Li-content, \( x \).

Figure 7(a) depicts the temperature dependence of the power factor \( P(T) \) of Li-doped CuO. As would be expected from the results of \( \rho(T) \) and \( S(T) \) values, the sample of \( x = 0.03 \) shows the highest performance, \( P = 1.6 \times 10^{-4} \) W K\(^{-2}\) m\(^{-1}\) at 1246 K, which is about one order of magnitude higher than that of the sample of \( x = 0.0005 \). Figure 7(b) shows the dimensionless figure of merit \( ZT \) of Li-doped CuO as a function of \( T \). The \( ZT \) value increases...
with increasing temperature and Li-content, $x$, and is the maximum value of $3.2 \times 10^{-2}$ with $x = 0.03$ at 1246 K.

Although $\kappa(T)$ decreased with increasing $x$ at low temperature, $\kappa(T)$ was independent of the Li-content at high temperature. As a result, the enhancement of the $ZT$ value at $x = 0.03$ results mainly from the large decrease in $\kappa(T)$ owing to carrier doping, and overcomes the decrease in $S(T)$. Another mechanism should be introduced for the reduction of $\kappa(T)$ at high temperature to enhance the $ZT$ value in the CuO system.

4. Summary
We have investigated the electrical and thermal properties of CuO polycrystals doped with alkali metals (Li, Na, K) and studied the potential of using CuO as a thermoelectric material. Important experimental results and conclusions obtained from this study are summarized as follows.

1) Among the alkali metals substituted into the Cu-site, Li$^+$ is the most promising ion for enhancing the thermoelectric performance. The Li ion replaced the
Cu-site or occupied the vacancy site of Cu. As a result, effective hole carriers were created.

2) For Li-doped (Cu\textsubscript{1-x}Li\textsubscript{x})O, the electrical resistivity $\rho(T)$ and Seebeck coefficient $S(T)$ decreased with increasing Li-content up to $x = 0.03$. Power factor $P(T) = S^2/\rho$ increases with increasing Li-content, is the maximum of $P = 1.6 \times 10^{-4}$ W K\textsuperscript{-2} m\textsuperscript{-1} at 1246 K with $x = 0.03$, and decreases in performance with further increase in $x$.

3) Thermal conductivity $\kappa(T)$ decreased with increasing Li-content up to $x = 0.03$ at $T < 300$ K. The $x$ value at 1200 K was estimated to be about 60 mW/cm K, which was independent of $x$. The dimensionless thermoelectric figure of merit $ZT = S^2T/\kappa$ increases with increasing Li-content, and is the maximum of $ZT = 3.2 \times 10^{-2}$ at 1246 K with $x = 0.03$. To enhance the $ZT$ value, another scattering center must be introduced.

4) In nondoped CuO, which was fabricated under the present conditions, the sign of $S(T)$ shows a reentrant behavior. The mechanism of sign change may come from the defect chemistry. The detailed study is in progress.

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