Thermoelectric Properties of $\text{CuAl}_{1-x}\text{M}_x\text{O}_2$ ($\text{M} = \text{Zn, Ca}$)

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Substitution was performed with Ca^{2+} and Zn^{2+} in the Al^{3+} site of CuAlO_2 . We investigated the influence of substitution on thermoelectric properties. Power factors were the highest near 850 K for the samples of $\text{CuAl}_{0.999}\text{Zn}_{0.001}\text{O}_2$ ($6.8 \times 10^{-5} \text{ W m}^{-1} \text{ K}^{-2}$), $\text{CuAl}_{0.999}\text{Ca}_{0.001}\text{O}_2$ ($7.4 \times 10^{-5} \text{ W m}^{-1} \text{ K}^{-2}$), CuAlO_2 ($6.6 \times 10^{-5} \text{ W m}^{-1} \text{ K}^{-2}$).

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1. Introduction

CuAlO_2 can be expected to have a high thermoelectromotive force as a thermoelectric material.^{4,5} However, its electrical conductivity is lower by 1/1000 than that of NaCo_2O_4 .¹ In order to utilize CuAlO_2 as a thermoelectric material it is necessary to improve its electric conductivity, because $Z (= \sigma \alpha^2 / \kappa)$, where σ is electrical conductivity, α is Seebeck coefficient, and κ is thermal conductivity) is required to have high thermoelectric properties. If σ becomes high by this system, thermoelectric efficiency increases.

Result of computer simulation of Yoshida *et al.*² showed the Al-vacancy impurity level (acceptor level), where the Ca^{2+} level was found to be above the Al-vacancy level. The experimental result of Katsui *et al.*^{3,6} shows an electrical conductivity which is higher than that of CuAlO_2 . In this research, polycrystalline $\text{CuAl}_{1-x}\text{M}_x\text{O}_2$ ($\text{M} = \text{Zn, Ca}$) was produced based on computer simulations, and we investigated the effects of Zn and Ca substitution on its thermoelectric properties.

2. Experimental Procedures

Cu_2O , Al_2O_3 and ZnO CaCO_3 powders were used as raw materials for solid-state reaction.^{6,7} These materials were mixed in a molar ratio of $\text{Al}_2\text{O}_3 : (\text{ZnO, CaCO}_3) = (1 - x) : x$ ($x = 0, 0.001, 0.01$) a planetary ball mill for 2 h. The mixed powders were calcined at 1373 K for 12 h. Then, Cu_2O was mixed with the calcined powder, and ball-milled for 24 h, palletized and calcined at 1373 K for 24 h. The sintered pellet was pulverized. Then it was milled for 24 h. The mixture was obtained at 245 (MPa) and sintered at 1473 K for 48 h. The sintered pellet was cut into rectangles and annealed at 1373 K for 24 h. Electrical conductivity and Seebeck coefficient were measured by the four-probe method, and thermal conductivity was measured by the laser flash method. Microstructures were observed by scanning electron microscopy (SEM) and phase and crystal structures were analyzed by X-ray diffraction (XRD) analysis.

3. Result and Discussion

Figure 1 shows the XRD pattern of polycrystalline

Fig. 1 XRD patterns for sintered $\text{CuAl}_{1-x}\text{M}_x\text{O}_2$ ($\text{M} = \text{Zn, Ca}$).

$\text{CuAl}_{1-x}\text{M}_x\text{O}_2$ ($\text{M} = \text{Zn, Ca}$). When Zn and Ca at $x = 0$ and 0.001 were added, single-phase CuAlO_2 was obtained. However, the $x = 0.01$ for both Zn and Ca yielded CuAlO_2 with impurity phase. This suggests that the added Zn and Ca reacted with Al_2O_3 in ZnAl_2O_4 and CaAl_2O_4 , and excess CuO and Cu_2O was crystallized as an oxide phase.

Figure 2 shows the lattice parameter dependence of Zn content (x) for $\text{CuAl}_{1-x}\text{Zn}_x\text{O}_2$ polycrystalline samples. In Fig. 2(a) the a -axis and c -axis length dependences of Zn content (x) are shown. The samples, a -axis parameters increase with increasing Zn content (x). Zn causes the length of the Al–O layer to become shorter because of its stronger ionicity. According to Koumoto *et al.*,^{4,5} $\alpha_{\parallel}$ indicated the biggest Seebeck coefficient due to the small length between layers. Figure 2(b) shows the Zn content (x) dependences of c/a and volume, where c/a decreases with Zn content (x). The reason for the Al–O layer to thin down is suggested to be that c -axis length decreases and a -axis length increases with Zn content (x).¹⁴

Figure 3 shows the dependences of Ca content (x) on

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Fig. 2 Lattice parameter of $\text{CuAl}_{1-x}\text{Zn}_x\text{O}_2$, (a) a -axis and c -axis, (b) c/a and volume.

lattice parameters for the $\text{CuAl}_{1-x}\text{Ca}_x\text{O}_2$ polycrystalline samples. Figure 3(a) shows the Ca content (x) dependences of the a -axis and c -axis. The a -axis parameter for $x = 0.01$ is larger than that for $x = 0.001$. For $x = 0.001$, the c -axis decreased markedly, but for $x = 0.01$ it increased slightly.

Figure 3(b) shows the Ca content (x) dependences of c/a and volume. The c/a for $x = 0.01$ was smaller than that for $x = 0.001$. For $x = 0.001$, c/a decreased markedly, but for $x = 0.001$ it decreased slightly.¹⁴⁾

SEM images of the sintered polycrystalline samples shown in Fig. 4. The SEM observations show the damaged surfaces. All the images show platy grains. Zn content (x) increases with increasing grain size. However, Ca content (x) increases with decreasing grain size. The cause of this is suggested to be the poor control of grain growth due to the formation of impurities.

Figure 5 shows the temperature dependence of electrical conductivity of $\text{CuAl}_{1-x}\text{M}_x\text{O}_2$ ($\text{M} = \text{Zn}, \text{Ca}$) polycrystalline samples. The roughly estimated activation energies (E_a) at the higher temperature region (K) in the Arrhenius plot $\log \sigma$ vs $1/T$, were 0.25 eV for CuAlO_2 ,^{10–12)} Zn $x = 0.001, 0.01$ and Ca $x = 0.01$. Temperature above 600 K did not show linearity in the Arrhenius plot $\log \sigma$ vs $1/T$, this is suggestion

Fig. 3 Lattice parameter of $\text{CuAl}_{1-x}\text{Ca}_x\text{O}_2$, (a) a -axis and c -axis, (b) c/a and volume.

influence carrier scattering in the grain boundary. The electrical conductivity σ at room temperature is 17.2 (Sm^{-1}) for Ca $x = 0.001$, which is the highest σ of all samples. There was a difference in electrical conductivity at approximately 500 K in all samples. However, this difference did not appear at temperatures higher than 500 K. Hole doping was carried out on the samples of Ca $x = 0.001$ to increase electrical conductivity. But, following to temperature increase, electrical conductivity had decreased. This is suggested that recombination was caused with electrons where holes are generated in excitation heat. As for all samples, electrical conductivity increases with temperature indicating semiconductor behavior.

Figure 6 shows the temperature dependence of Seebeck coefficient for $\text{CuAl}_{1-x}\text{M}_x\text{O}_2$ ($\text{M} = \text{Zn}, \text{Ca}$) polycrystalline samples. The Seebeck coefficient α at room temperature is approximately 870 (μVK^{-1}) for all samples. As for all samples, with increasing temperature Seebeck coefficient decreased, but at above approximately 650 K the Seebeck coefficient is negligible. From the fact that the Seebeck

Fig. 4 SEM images of sintered $\text{CuAl}_{1-x}\text{M}_x\text{O}_2$ ($M = \text{Zn}$ and Ca) polycrystalline samples.

coefficient is positive, all samples are p-type semiconductors.

Figure 7 shows the temperature dependence of thermal conductivity for $\text{CuAl}_{1-x}\text{M}_x\text{O}_2$ (Zn , Ca) polycrystalline samples. The thermal conductivity κ of Zn $x = 0.01$ at room temperature is approximately 10 times that of conventional oxides. Following to temperature increase it decreased thermal conductivity. For Zn $x = 0.001$, the thermal conductivity of approximately $5 (\text{Wm}^{-1}\text{K}^{-1})$ as the lowest in all samples. Thermal conductivity increased with Zn content based on the grain size as shown in the SEM image in Fig. 4. Zn $x = 0.01$. Also, the fact that it increased with increasing amount of impurities is the cause of Zn $x = 0.01$ according to XRD analysis. Even in the case of Ca $x = 0.01$, the existence of the impurities was verified by the decrease in thermal

Fig. 5 Temperature dependence of electrical conductivity (σ) of sintered $\text{CuAl}_{1-x}\text{M}_x\text{O}_2$ ($M = \text{Zn}$, Ca) polycrystalline samples.

Fig. 6 Temperature dependence of Seebeck coefficient (α) of sintered $\text{CuAl}_{1-x}\text{M}_x\text{O}_2$ ($M = \text{Zn}$, Ca) polycrystalline samples.

conductivity with increasing temperature. The reason the $\text{Zn} = 0.01$ sample had a larger κ was suggested to be that there might exist impurities such as ZnAl_2O_4 ($25 \text{ Wm}^{-1}\text{K}^{-1}$ 300 K) possessing a larger thermal conductivity.⁹⁾ Furthermore, the case of $\text{Zn} = 0.001$ showed the lowest κ and one forth that of the case of $\text{Zn} = 0.01$ at 400 K. In addition, κ for $\text{Zn} = 0.001$ decreased with increasing temperature up to 850 K. We found the optimum amount of Zn required to decrease κ , which was not regarded to form ZnO . This is the main difference between Zn and Ca .

The figures of merits of the samples of $\text{CuAl}_{1-x}\text{M}_x\text{O}_2$ ($M = \text{Zn}$, Ca) are shown in Fig. 8. The largest one in the case of $\text{Zn} = 0.001$ was $1.3 \times 10^{-5} \text{ K}^{-1}$ at approximately 850 K,

Fig. 7 Temperature dependence of thermal conductivity (κ) of sintered $\text{CuAl}_{1-x}\text{M}_x\text{O}_2$ ($\text{M} = \text{Zn}, \text{Ca}$) polycrystalline samples.

Fig. 8 Temperature dependence of figure of merit (Z) of sintered $\text{CuAl}_{1-x}\text{M}_x\text{O}_2$ ($\text{M} = \text{Zn}, \text{Ca}$) polycrystalline samples.

which was only one order larger than that in the case of CuAlO_2 . These figures of merit were 10 times larger than those of the other oxide because of the larger thermal conductivity. The power factors, PFs, at approximately 850 K are $x = 0$; 6.6×10^{-5} , Zn $x = 0.001$; 6.8×10^{-5} , Zn $x = 0.01$; 6.8×10^{-5} , Ca $x = 0.001$; 7.4×10^{-5} , Ca $x = 0.01$; 7.2×10^{-5} ($\text{Wm}^{-1}\text{K}^{-2}$).

4. Conclusion

The electrical conductivities of the substituted samples (Zn and Ca) were almost the same. Even in terms of temperature dependence and did not improve compared with the CuAlO_2 . However, the sample of Zn = 0.001 had a decreased thermal conductivity of 5 ($\text{Wm}^{-1}\text{K}^{-1}$) at approximately 800 K, which showed a decrease in $\text{CuAl}_{0.999}\text{Zn}_{0.001}\text{O}_2$ with increasing temperature. The resulting figure of merit was 1.3×10^{-5} (K^{-1}). This figure of merit is approximately 1.7 times better than the 7.5×10^{-6} (K^{-1}) of CuAlO_2 .

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