Thermoelectric Properties of Zn$_{1-(x+y)}$Ga$_x$In$_y$O ($x + y = 0.007$) System

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Abstract

The intermetallic compounds which are mainly used for the thermoelectric power generation system are unstable at high temperature. Therefore, we studied thermoelectric property of ZnO doped with group 13 elements, which can be expected to be a good candidate of thermoelectric material with high performance. The electrical conductivity ($\sigma$) and Seebeck coefficient (S) were evaluated under He atmosphere from 673 K to 1073 K. Power factor ($S^2\sigma$) of Zn$_{9.993}$Ga$_{0.0023}$In$_{0.0047}$O showed higher value than that of Zn$_{9.993}$A$_{0.007}$O (A = Ga, In). Thus, the multi cation-doping was effective for the improvement of power factor.

Keywords: Zn$_{1-(x+y)}$Ga$_x$In$_y$O; electrical conductivity; seebeck coefficient; average ionic radius; thermoelectric material

1. Introduction

The development of next power generation systems such as solar cell, thermoelectric generation, solid oxide fuel cell, etc., is demanded due to the exhaustion problem of fossil fuel. Among them, we are interested in the thermoelectric power generation. Although intermetallic compounds are mainly used as thermoelectric material, they are not stable at high temperatures in air. Therefore, we studied n-type oxide semiconductor ZnO which can be expected to be a good candidate of thermoelectric material with high performance. Recently, 1-2 mol% Al doped ZnO which has been studied as the transparent electrode material, has been reported to be an excellent n-type thermoelectric oxide material. [1-2] On the other hand, our research group has reported that the Ga and In co-doped ZnO system showed the minimum resistivity around the average ionic radius of 0.054 nm.[3] In the present study, it was tried to apply the multi cation-doped ZnO to the thermoelectric material.
2. Experimental

\( \text{Zn}_{1-(x+y)} \text{Ga}_{x} \text{In}_{y} \text{O} \ (x+y = 0.007) \) systems were prepared by solid-state reaction method, using ZnO (99.999 %, Koujundo chemical), \( \text{Ga}_{2}\text{O}_{3} \) (99.9 %, Koujond chemical), and \( \text{In}_{2}\text{O}_{3} \) (99.99 %, Koujundo chemical) as starting reagents. The average ionic radius of dopant (\( r_{av} \)) was calculated by using eq. (1)

\[
r_{av} = r_1 \times (x / x + y) + r_2 \times (y / x + y),
\]

where \( r_1 \) and \( r_2 \) are the dopant ionic radius, and \( x \) and \( y \) are the molar concentration of the dopant component. Ionic radii of \( \text{Zn}^{2+}, \text{Ga}^{3+}, \) and \( \text{In}^{3+} \) by Shannon [4] are summarized in Table 1. The relationship between \( r_{av} \) and composition of \( \text{Zn}_{1-(x+y)} \text{Ga}_{x} \text{In}_{y} \text{O} \) system is summarized in Table 2. Since the total concentration of the dopant was controlled to be 7 mmol, the molar concentration of the dopant component was estimated by varying the range of \( 0 \leq x \leq 0.007 \) and \( 0 \leq y \leq 0.007 \). The starting reagents were weighted by using a weighing bottle and were mixed in ball mill for 24 h. The mixed powders were calcined at 1073 K for 5 h. After the calcination, the mixed powders were pressed into a rectangular-shaped specimen, and then sintered at 1673 K for 10 h in air. The sintered samples were analyzed by X-ray powder diffraction (XRD) (Multiflex, Rigaku) using Cu K\( \alpha \) radiation at room temperature. Seebeck coefficient and electrical conductivity of samples were measured using ZEM-3 (ULVAC, Japan) under He atmosphere from 673 K to 1073K. The power factor was calculated by using the electrical conductivity and Seebeck coefficient.

3. Results and discussion

3.1. XRD

The XRD patterns of \( \text{Zn}_{1-(x+y)} \text{Ga}_{x} \text{In}_{y} \text{O} \) system are shown in Fig. 1. The XRD patterns of \( \text{Zn}_{1-(x+y)} \text{Ga}_{x} \text{In}_{y} \text{O} \) system (\( x + y = 0.007 \)) were assigned to be a single phase of hexagonal ZnO. The relative densities of all the sintered specimens were 95 % for X-ray density. The lattice parameters of \( \text{Zn}_{1-(x+y)} \text{Ga}_{x} \text{In}_{y} \text{O} \) system are shown in Fig. 2. The a-axis increased with increasing \( r_{av} \), while the c-axis scattered. The c/a lattice ratios of \( \text{Zn}_{1-(x+y)} \text{Ga}_{x} \text{In}_{y} \text{O} \) system are shown in Fig. 3. In spite of scattering in c-axis, the c/a lattice ratio tends to decrease with increasing \( r_{av} \).
3.2. Electrical properties

Figure 4 represents the electrical conductivity as a function of temperature. The conductivity of co-doped system was higher than that of single doped system and showed the maximum value in the sample with $r_{av} = 0.054$ nm. Figure 5 shows the Seebeck coefficient as a function of temperature. The Seebeck coefficient of samples increased linearly with increase in the temperature. The Seebeck coefficient of the sample with $r_{av} = 0.057$ nm showed the highest value ($151 \times 10^{-6} \text{VK}^{-1}$ at 1073 K) among the co-doped systems. On the other ward, $\text{Zn}_{0.993}\text{In}_{0.007}\text{O}$ showed highest value ($157 \times 10^{-6} \text{VK}^{-1}$ at 1073K) in single
doped system. The electrical conductivity (\( \sigma \)) and the Seebeck coefficient (S) is given by the following equations:

\[
\sigma = e n \mu, \quad \tag{2}
\]

\[
S = \frac{\dot{S}}{k_B/e} \left[ (r + 2) + \ln \left\{ 2 \pi m^* k_B T^{3/2} / h^3 n \right\} \right], \quad \tag{3}
\]

where \( \mu, k_B, e, r, m^*, h, \) and \( n \) represent the mobility of conduction carrier, the Bolzmann’s constant, the elementary electric charge, the scattering parameter, the effective mass, Planck’s constant and currer concentration, respectively. According to the equation 2 and 3, it is well known that the increase in conduction carrier increases the electrical conductivity, but decreases the Seebeck coefficient. In this study, however, the Seebeck coefficient did not change regardless of the increase in the electrical conductivity, when they were compared at a given temperature. Therefore, it was considered that the carrier concentration did not change. Figure 6 shows the Seebeck coefficient as a function of the electrical conductivity. Although the Seebeck coefficient did not change for all samples, the line of \( \sigma – S \) plot for the co-doped system shifted to the right side as compared with single doped system. It is thought that the carrier mobility for the co-doped system increased as compared with the single doped system. The improvement of carrier mobility may be ascribed to the decrease in the crystal lattice strain which caused by co-doping.

![Image](image1.png)

**Fig. 5** The Seebeck coefficient of Zn\(_{1-(x+y)}\)Ga\(_x\)In\(_y\)O system (\( x + y = 0.007, 0 \leq x \leq 0.007, 0 \leq y \leq 0.007 \)) as a function of temperature for \( r_{av} = 0.048 \) nm ( ), 0.051 nm ( ), 0.054 nm ( ), 0.057 nm ( ), 0.060 nm ( ), Zn\(_{0.993}\)Ga\(_{0.007}\)O ( ), Zn\(_{0.993}\)In\(_{0.007}\)O ( )

![Image](image2.png)

**Fig. 6** The \( \sigma – S \) plot of Zn\(_{1-(x+y)}\)Ga\(_x\)In\(_y\)O system (\( x + y = 0.007, 0 \leq x \leq 0.007, 0 \leq y \leq 0.007 \)) for \( r_{av} = 0.048 \) nm ( ), 0.051 nm ( ), 0.054 nm ( ), 0.057 nm ( ), 0.060 nm ( ), Zn\(_{0.993}\)Ga\(_{0.007}\)O ( ), Zn\(_{0.993}\)In\(_{0.007}\)O ( ).

### 3.3. Power factor

The calculated values of \( S^2 \sigma \) for ZnO and Zn\(_{1-(x+y)}\)Ga\(_x\)In\(_y\)O are shown in Figure 7. The \( S^2 \sigma \), which is generally called power factor, represents the electrical contribution to the overall thermoelectric performance. The \( S^2 \sigma \) values for all the samples increased with increasing temperature. The power factors of Zn\(_{1-(x+y)}\)Ga\(_x\)In\(_y\)O with \( r_{av} = 0.054 \) and 0.057 nm at 1073 K were estimated to be 6.6 and 7.0 \( \times 10^{-4} \) W m\(^{-1}\) K\(^{-1}\), respectively. These values were higher than those of single cation doped ZnO such as Zn\(_{0.993}\)Ga\(_{0.007}\)O or Zn\(_{0.993}\)In\(_{0.007}\)O, which were 6.2 or 5.5 \( \times 10^{-4} \) W m\(^{-1}\) K\(^{-1}\) at 1073 K, respectively. Wiff et al. [5], reported that the decrease in c/a value enhanced the power factor. In this study, the power factor of Zn\(_{1-} \)
(x+y)GaInO with $r_{av} = 0.057$ nm, of which the c/a value showed the minimum value, showed the maximum value among the co-doped system. This fact agreed with the results of Wiff et al. Therefore, the co-doping into ZnO was effective for the improvement of the power factor.

4. Conclusions

The Ga and In co-doped ZnO ($\text{Zn}_{1-(x+y)}\text{Ga}_x\text{In}_y\text{O}$) samples showed a single phase of hexagonal ZnO. The co-doping was effective for the improvement of electrical conductivity than single doped ZnO. The Seebeck coefficient of sample with $r_{av} = 0.048$ nm (●), 0.051 nm (■), 0.054 nm (◆), 0.057 nm (▲), 0.060 nm (▼) $\text{Zn}_{0.993}\text{Ga}_{0.007}\text{O}$ (△), $\text{Zn}_{0.993}\text{In}_{0.007}\text{O}$ (○).

Fig. 7 The power factor of $\text{Zn}_{1-(x+y)}\text{Ga}_x\text{In}_y\text{O}$ system ($x + y = 0.007$, $0 \leq x \leq 0.007$, $0 \leq y \leq 0.007$) as a function of temperature for $r_{av} = 0.048$ nm (●), 0.051 nm (■), 0.054 nm (◆), 0.057 nm (▲), 0.060 nm (▼), $\text{Zn}_{0.993}\text{Ga}_{0.007}\text{O}$ (△), $\text{Zn}_{0.993}\text{In}_{0.007}\text{O}$ (○).

The power factor of $\text{Zn}_{1-(x+y)}\text{Ga}_x\text{In}_y\text{O}$ was estimated from the observed value of electrical conductivity and Seebeck coefficient. The power factors of $\text{Zn}_{1-(x+y)}\text{Ga}_x\text{In}_y\text{O}$ with $r_{av} = 0.054$ and 0.057 nm at 1073 K were estimated to be 6.6 and 7.0×$10^{-4}$ Wm$^{-1}$K$^{-2}$, respectively. These values were higher than those of single cation doped ZnO such as $\text{Zn}_{0.993}\text{Ga}_{0.007}\text{O}$ or $\text{Zn}_{0.993}\text{In}_{0.007}\text{O}$, which were 6.2 or 5.5×$10^{-4}$ Wm$^{-1}$K$^{-2}$ at 1073 K, respectively. Therefore, the co-doping into ZnO was effective for the improvement of the power factor.

References