Lattice distortion and thermoelectric property for $\text{Zn}_{1-(x+y)}\text{Ga}_x\text{In}_y\text{O}$ system ($x + y = 0.007$, $0 \leq x \leq 0.007$, $0 \leq y \leq 0.007$)

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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 3B elements periodic table, which can be expected to be a good candidate of thermoelectric material with high performance. The electrical conductivity (σ) and Seebeck coefficient (S) were evaluated under He atmosphere from 673 to 1073K. Although the electrical conductivity was showed maximum value for sample with $r_{\text{av.}} = 0.054$ nm, the Seebeck coefficient did not change for all samples. This fact was considered that the increase in electrical conductivity was caused by improvement of carrier mobility, and the improvement of carrier mobility may be ascribed to the decrease in lattice distortion which caused by co-doping. Power factor ($S^2\sigma$) of $\text{Zn}_{0.993}\text{Ga}_{0.0023}\text{In}_{0.0047}\text{O}$ showed higher value than that of $\text{Zn}_{0.993}\text{A}_{0.007}\text{O}$ (A = Ga, In). Thus, the co-doping was effective for the improvement of power factor.

Key word : $\text{Zn}_{1-(x+y)}\text{Ga}_x\text{In}_y\text{O}$, electrical conductivity, Seebeck coefficient, ionic radius, lattice distortion

1 Introduction

Recently, the development of next generation energy systems is desired due to the exhaustion problem of fossil fuel. As a consequence of this, the thermoelectric generation system is focused. However, the system can be used in the limited temperature range (from 300K to 700K) because of use of the intermetallic alloys such as PbTe [1] and $\text{Bi}_2\text{Te}_{2.85}\text{Se}_{0.15}$ [2]. To overcome this limited temperature problem, thermoelectric properties of ZnO which has high thermal stability in the temperature ranging from 600K to 1100K has been examined for development of high quality thermoelectric materials. Tsubota et al and Fujishiro et al reported that Al (1 to 2mol%) doped ZnO developed as transparent electrode material showed excellent n-type thermoelectric properties.[3-4] Also, our research group has reported that the Ga and In co-doped ZnO system showed the minimum resistivity around the mean ionic radius of 0.054 nm.[5] In the present work, the relationship among the mean ionic radius of Zn site in co-doped system, lattice distortion ($\Delta d/d$), and power factor ($S^2\sigma$) was examined for development design paradigm for fabrication of high quality ZnO thermoelectric material.

2 Experimental

$\text{Zn}_{1-(x+y)}\text{Ga}_x\text{In}_y\text{O}$ ($x+y=0.007$) compounds were prepared by using solid-state reaction method. The starting materials used were ZnO powder (99.999 %, Koujundo chemical co ltd.), Ga_2O_3 powder (99.9 %, Koujond chemical co ltd.), and In_2O_3 powder (99.99 %, Koujundo chemical co ltd.). The mean ionic radius of dopant ($r_{\text{av.}}$) was calculated by using Equation (1)

$$r_{\text{av.}} = r_1 \times (x / x + y) + r_2 \times (y / x + y), \quad (1)$$

where r_1 and r_2 are the dopant ionic radius, and x and y are the molar concentration of the dopant component. The ionic radii of Zn^{2+} , Ga^{3+} , and In^{3+} which were estimated as four oxygen coordination around cations by Shannon [6] are presented in Table 1. The relationship between $r_{\text{av.}}$ and composition of $\text{Zn}_{1-(x+y)}\text{Ga}_x\text{In}_y\text{O}$ are summarized in Table 2. The total amount of dopant in composition of $\text{Zn}_{1-(x+y)}\text{Ga}_x\text{In}_y\text{O}$ was fixed to 0.007. The compositions of examined samples shown in Table 2. The starting reagents were weighted by using a weighing bottle and were mixed in ball mill for 24h. The mixed powders were calcined at 1073K, 5h. After the calcination, the mixed powders were pressed into a rectangular-shaped specimen, and sintered at 1673K, 10h in air. The crystal phases of sintered samples were identified at room temperature by using X-ray powder diffraction (XRD, Multiflex, Rigaku Company) equipment. In order to calculate the lattice distortions of samples, the structural parameters of samples were refined using Rietveld analysis [7]. The Seebeck coefficient and the electrical conductivity of samples were measured using ZEM-3 (ULVAC, Japan) under He atmosphere from 673 to 1073K. The power factor was calculated by using the electrical conductivity and Seebeck coefficient.

Table 1 Ionic radius in tetrahedrally coordination.

ion	ionic radius / nm
Zn^{2+}	0.060
Ga^{3+}	0.047
In^{3+}	0.062

3 Results and discussion

3.1 XRD

The XRD patterns observed for $Zn_{1-(x+y)}Ga_xIn_yO$ sintered samples are shown in Fig.1. The figure indicates that all observed samples consist of single phase of hexagonal ZnO and no other phases are observed. The relative densities which were measured using all sintered samples were more than 95% to theoretical one which was calculated by using lattice constants and crystallographic data.

Table 2 The relationship between r_{av} and composition of $Zn_{1-(x+y)}Ga_xIn_yO$ ($x+y=0.007$) system.

composition	mean ionic radius (r_{av})/nm
$Zn_{0.993}Ga_{0.007}O$	0.047
$Zn_{0.993}Ga_{0.0065}In_{0.0005}O$	0.048
$Zn_{0.993}Ga_{0.0051}In_{0.0019}O$	0.051
$Zn_{0.993}Ga_{0.0037}In_{0.0033}O$	0.054
$Zn_{0.993}Ga_{0.0023}In_{0.0047}O$	0.057
$Zn_{0.993}Ga_{0.0009}In_{0.0061}O$	0.060
$Zn_{0.993}In_{0.007}O$	0.062

Fig.3 The Seebeck coefficient 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 ($\bullet$), 0.051 nm ($\blacksquare$), 0.054 nm ($\blacklozenge$), 0.057 nm ($\blacktriangle$), 0.060 nm ($\blacktriangledown$), $\text{Zn}_{0.993}\text{Ga}_{0.007}\text{O}$ (Δ), $\text{Zn}_{0.993}\text{In}_{0.007}\text{O}$ ($\circ$).

Fig.4 The Seebeck coefficient 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 electrical conductivity for $r_{av} = 0.048$ nm ($\bullet$), 0.051 nm ($\blacksquare$), 0.054 nm ($\blacklozenge$), 0.057 nm ($\blacktriangle$), 0.060 nm ($\blacktriangledown$), $\text{Zn}_{0.993}\text{Ga}_{0.007}\text{O}$ (Δ), $\text{Zn}_{0.993}\text{In}_{0.007}\text{O}$ ($\circ$).

3.3 $\beta \cos \theta - \sin \theta$ plot

$\beta \cos \theta - \sin \theta$ plot was used to estimate the lattice distortion ($\Delta d/d$) in observed samples. In case of co-doped system, the full width at half maximum (FWHM) of XRD patterns observed for co-dope samples become broad or narrow due to the change of crystalline size and lattice distortion. Therefore, the observed FWHM of XRD pattern can be expressed by the following Equation (4).

$$\beta = \beta_c + \beta_s \quad (4)$$

where β , β_c and β_s present the observed FWHM of

X-ray diffraction pattern, the FWHM of XRD pattern by crystallite with distortion free and the FWHM of XRD pattern by crystallite with lattice distortion, respectively. The β_c is expressed by using Equation (5) (i.e. Scherrer's Equation):

$$\beta_c = K\lambda / D \cos \theta \quad (5)$$

where K , λ , D , and θ presents Scherrer constant, wavelength of X-ray source, crystallite size, and Bragg angle, respectively. The β_s is shown the following equation by Bragg's equation:

$$\beta_s = (\Delta d/d) \sin \theta / \cos \theta \quad (6)$$

where $\Delta d/d$ and θ presents lattice distortion and Bragg angle. Therefore, Equation (4) can convert to Equation (7).

$$\beta \cos \theta = (\Delta d/d) \sin \theta + K\lambda / D \quad (7)$$

Figure 5 presents $\beta \cos \theta - \sin \theta$ plot for $\text{Zn}_{1-(x+y)}\text{Ga}_x\text{In}_y\text{O}$ system ($x+y=0.007$). The FWHM values which were estimated by Rietveld analysis [7] were used for the calculation of β values. This figure clearly indicates that $\beta \cos \theta - \sin \theta$ plot shows high linearity and lattice distortion can be correctly estimated using the observed data in Fig.5. Figure 6 demonstrates the relationship between lattice distortion ($\Delta d/d$) and mean ionic radii (r_{av}) observed for the samples. The lattice distortion values observed for samples which r_{av} values become 0.048 and 0.054 nm reached minimum in all observed lattice distortion values. Figure 7 shows the electrical conductivity as a function of $\Delta d/d$. From the result of Fig.7, the electrical conductivity tends to increase with decreasing lattice distortion. Based on all observed results, it is concluded that the carrier mobility is enhanced by a lowering of lattice distortion and the electrical conductivity is also improved by aforementioned enhancement of carrier mobility in the samples.

Fig.5 The $\beta \cos \theta - \sin \theta$ plot of $\text{Zn}_{1-(x+y)}\text{Ga}_x\text{In}_y\text{O}$ system by Rietveld analysis ($x+y=0.007$, $0 \leq x \leq 0.007$, $0 \leq y \leq 0.007$) as a function of electrical conductivity for $r_{av} = 0.048$ nm ($\bullet$), 0.051 nm ($\blacksquare$), 0.054 nm ($\blacklozenge$), 0.057 nm ($\blacktriangle$), 0.060 nm ($\blacktriangledown$), $\text{Zn}_{0.993}\text{Ga}_{0.007}\text{O}$ (Δ), $\text{Zn}_{0.993}\text{In}_{0.007}\text{O}$ ($\circ$).

Fig.6 The relationship between mean ionic radius and lattice distortion ($\Delta d/d$) for $\text{Zn}_{1-(x+y)}\text{Ga}_x\text{In}_y\text{O}$ system ($x+y=0.007$, $0 \leq x \leq 0.007$, $0 \leq y \leq 0.007$).

Fig.7 The relationship between electrical conductivity (at 673K (●) and 1073K (■)) and lattice distortion ($\Delta d/d$) for $\text{Zn}_{1-(x+y)}\text{Ga}_x\text{In}_y\text{O}$ system ($x+y=0.007$, $0 \leq x \leq 0.007$, $0 \leq y \leq 0.007$) with various ionic radii.

3.4 Power factor

The calculated values of $S^2\sigma$ for ZnO and $\text{Zn}_{1-(x+y)}\text{Ga}_x\text{In}_y\text{O}$ samples are shown in Fig.8. The $S^2\sigma$, which is generally called power factor, shows the electrical contribution to the overall thermoelectric performance. The $S^2\sigma$ values for all the samples increased with increasing temperature. The power factors calculated for $\text{Zn}_{1-(x+y)}\text{Ga}_x\text{In}_y\text{O}$ samples which r_{av} values become 0.054 and 0.057 nm were 6.6×10^{-4} and $7.0 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$ at 1073K, respectively. Those values were higher than the calculated power factors for single cation dope $\text{Zn}_{0.993}\text{Ga}_{0.007}\text{O}$ (power factor: $6.2 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$ at 1073K) and single cation dope $\text{Zn}_{0.993}\text{In}_{0.007}\text{O}$ (power factor: $5.5 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$ at

1073K). This result clearly indicates that co-doping of Ga and In cations into ZnO lattice is effective for the improvement of the power factors of ZnO system.

Fig.8 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 electrical conductivity for $r_{av} = 0.048 \text{ nm}$ (●), 0.051 nm (■), 0.054 nm (◆), 0.057 nm (▲), 0.060 nm (▼), $\text{Zn}_{0.993}\text{Ga}_{0.007}\text{O}$ (Δ), $\text{Zn}_{0.993}\text{In}_{0.007}\text{O}$ (○).

4 Conclusions

The Ga and In co-doped ZnO ($\text{Zn}_{1-(x+y)}\text{Ga}_x\text{In}_y\text{O}$) samples consisted of single phase of hexagonal ZnO. The co-doping was effective way for the improvement of electrical conductivity in ZnO system. The electrical conductivity in co-dope system was higher than that of single dope system. The Seebeck coefficient observed for $\text{Zn}_{0.993}\text{Ga}_{0.0023}\text{In}_{0.0047}\text{O}$ which r_{av} is equal to 0.057 nm was the highest (i.e. $151 \times 10^{-6} \text{ V K}^{-1}$ at 1073K) in all examined co-dope samples. Although the electrical conductivity of co-doped systems were higher than single doped system, the Seebeck coefficient showed almost the same value as the single doped system. This result indicates that the carrier mobility in co-dope samples is higher than that in the single dope samples. And the improvement of carrier mobility would be attributable to a lowering of lattice distortion by means of co-doping of Ga and In cations into ZnO lattice. To conclude the relationship between lattice distortion and electrical conductivity, the lattice distortion was calculated by using $\beta \cos \theta - \sin \theta$ plot. This analysis indicates that $\text{Zn}_{0.993}\text{Ga}_{0.0051}\text{In}_{0.0019}\text{O}$ (r_{av} : 0.048 nm) and $\text{Zn}_{0.993}\text{Ga}_{0.0037}\text{In}_{0.0033}\text{O}$ (r_{av} : 0.054 nm) show the lowest lattice distortion in all examined samples. Also the improvement of electrical conductivity corresponds to a lowering of lattice distortion and aforementioned two samples show higher electrical conductivity as compared with other examined samples. Based on all observed results, it is concluded that the carrier mobility is enhanced by a lowering of lattice distortion. Moreover, the power factors of $\text{Zn}_{1-(x+y)}\text{Ga}_x\text{In}_y\text{O}$ were calculated by using electrical conductivity and Seebeck coefficient. The power factors calculated for

$\text{Zn}_{0.993}\text{Ga}_{0.0037}\text{In}_{0.0033}\text{O}$ (r_{av} : 0.054nm) and $\text{Zn}_{0.993}\text{Ga}_{0.0023}\text{In}_{0.0047}\text{O}$ (r_{av} : 0.057nm) were 6.6×10^{-4} and $7.0 \times 10^{-4} \text{ Wm}^{-1}\text{K}^{-2}$ at 1073K, respectively. The aforementioned values were higher than single dope $\text{Zn}_{0.993}\text{Ga}_{0.007}\text{O}$ (power factor: $6.2 \times 10^{-4} \text{ Wm}^{-1}\text{K}^{-2}$ at 1073K) and $\text{Zn}_{0.993}\text{In}_{0.007}\text{O}$ (power factor: $5.5 \times 10^{-4} \text{ Wm}^{-1}\text{K}^{-2}$ at 1073K). This clearly indicates that the co-doping of Ga and In cation into ZnO lattice was effective for the improvement of the power factor.

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