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Processing and Characterization of ZnO-based Thermoelectric Materials

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***Abstract*— The thermoelectric performance of oxide materials has rapidly progressed recently due to their good chemical stability for high-temperature applications. In the present work, an attempt to understand the effect of Ga content on thermoelectric properties of the Al- and Ga-doped ZnO ceramics was made. Dually Al- and Ga-doped ZnO ceramics were produced via a conventional powder metallurgy route. The phase purity, the microstructure and the thermoelectric properties of the produced samples were then characterized. The correlation between the composition and the microstructure and the thermoelectric properties was investigated.**

***Keywords*— Thermoelectric, Dual doping, ZnO, Ceramic, Oxide**

I. INTRODUCTION

Nowadays, thermoelectric materials are attracting renewed interests due to their high potential of recovering waste heat to generate electricity [1]. In particular, ceramic thermoelectric materials have been paid more attention as promising candidates for energy conversion at high temperature because of their advantages, such as non-toxic, thermally stable and highly resistive to oxidation at high temperature compared to those of metallic-based thermoelectric materials [2], [3].

Recently, ZnO-based oxide has been taken into consideration as an alternative n-type thermoelectric oxide material because of their high melting point, good chemical stability, high electrical conductivity and high Seebeck coefficient [4]. It has been reported that the thermoelectric properties of ZnO were enhanced with the introduction of the dopants such as Al and Ga [5]. Ohtaki et al [6], [7] reported that the dimensionless figures of merit ZT of this material with Al doping were 0.3 at 1000 ^{o}C and 0.65 at 974 ^{o}C by dual Al- and Ga-doping. It was suggested that the solubility limit of Al in ZnO was extended by introducing Ga resulting in enhancement of the thermoelectric performance [7]. On the other hand, Wiff et al [8] indicated that the deterioration of the thermoelectric properties was observed for Ga-doped ZnO.

In the present work, dually Al- and Ga-doped ZnO were produced via a powder metallurgy method. For the produced materials, the phase purity, the microstructure and the temperature-dependent thermoelectric properties were characterized. The correlation between the composition (the Ga content) as well as the microstructure and the thermoelectric parameters was investigated.

II. EXPERIMENTAL PROCEDURE

$Zn_{0.96}Al_{0.02}(Ga_{0.02})_xO$ (x = 0.2, 0.6, 1 and 1.4) samples were prepared via a solid-state reaction of ZnO, γ-Al_2O_3 and Ga_2O_3 powders (Alfa Aesar). The three powders were weighed according to the designed compositions and ball milled for 24 hours at a rotation speed of 25 rpm to obtain a particle size of 2 μm. The milled powders were calcined at 1100 ^{o}C for 5 hours in nitrogen using a Scan-therm tube furnace. The calcined powders were crushed up and sieved for pellet pressing. A Hawe die pressing machine and a Sten 100 cold isostatic pressing machine were used to press to obtain the green compacts, and the applied pressures were 40 and 2000 MPa, respectively. The pressed pellets were subjected to sintering at 1400 ^{o}C for 5 hours in nitrogen using the same tube furnace as for calcination.

For the sintered samples, the density was obtained by measuring the geometry and the weight. A Bruker D8 XRD with Cu K_α radiation and a Supra 35 SEM were employed to investigate the phase purity and the microstructure, respectively. The electrical conductivity and the Seebeck coefficient were measured by a ZEM-3 testing apparatus in a low pressure of helium with a temperature range from room temperature to 900 ^{o}C. The thermal conductivity was measured in air using a Netzsch LFA 457 Microflash from room temperature to 900 ^{o}C.

III. RESULTS AND DISCUSSION

Table I gives the density results of the prepared samples. As seen from this table, the density seems to decrease with increasing the content of Ga. Compared to the relatively low density (88% of theoretical density) of the ZnAlGa4O, high densities (94-96% of theoretical density) were achieved for other three samples.

The XRD diagrams of the calcined powders and the sintered compacts are shown in Figure 1. In Figure 1a, all the calcined powders show pure ZnO with the wurtzite structure. After sintering, the peaks of the materials mainly correspond to the ZnO. In addition, a noticeable peak in the higher Ga-containing samples (x = 1 and 1.4) occurs, and also its intensity increases with increasing the Ga content (see the solid cricle in Figure 1b). Ohtaki et al [7] reported that this peak was considered as an impurity phase containing Ga.

The SEM images of the fracture surfaces of the sintered samples are shown in Figure 2. It seems that the grain size

decreases with increasing the content of Ga. In addition, the sample of ZnAlGa4O shows more porous structure with the increased Ga content. The SEM observation is consistent with the density measurement.

TABLE I

DENSITY RESULTS OF THE PREPARED SAMPLES

Name	Composition	Density (g/cm^3)
ZnAlGa1O	$Zn_{0.96}Al_{0.02}(Ga_{0.02})_{0.2}O$	5.36
ZnAlGa2O	$Zn_{0.96}Al_{0.02}(Ga_{0.02})_{0.6}O$	5.27
ZnAlGa3O	$Zn_{0.96}Al_{0.02}Ga_{0.02}O$	5.24
ZnAlGa4O	$Zn_{0.96}Al_{0.02}(Ga_{0.02})_{1.4}O$	4.90

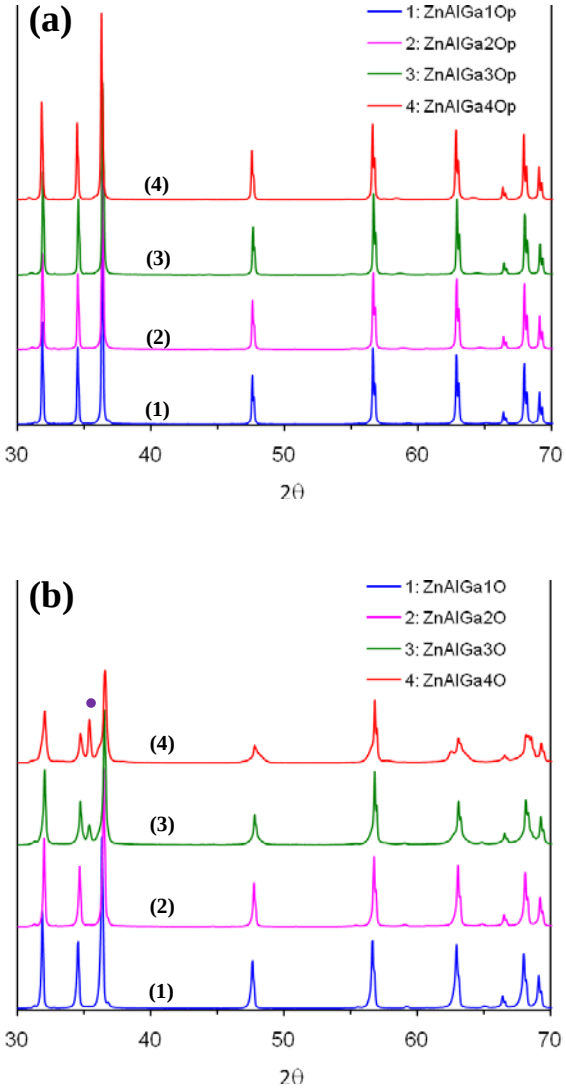

Fig. 1 XRD diagrams of Al- and Ga-doped ZnO: (a) calcined powders (b) sintered samples

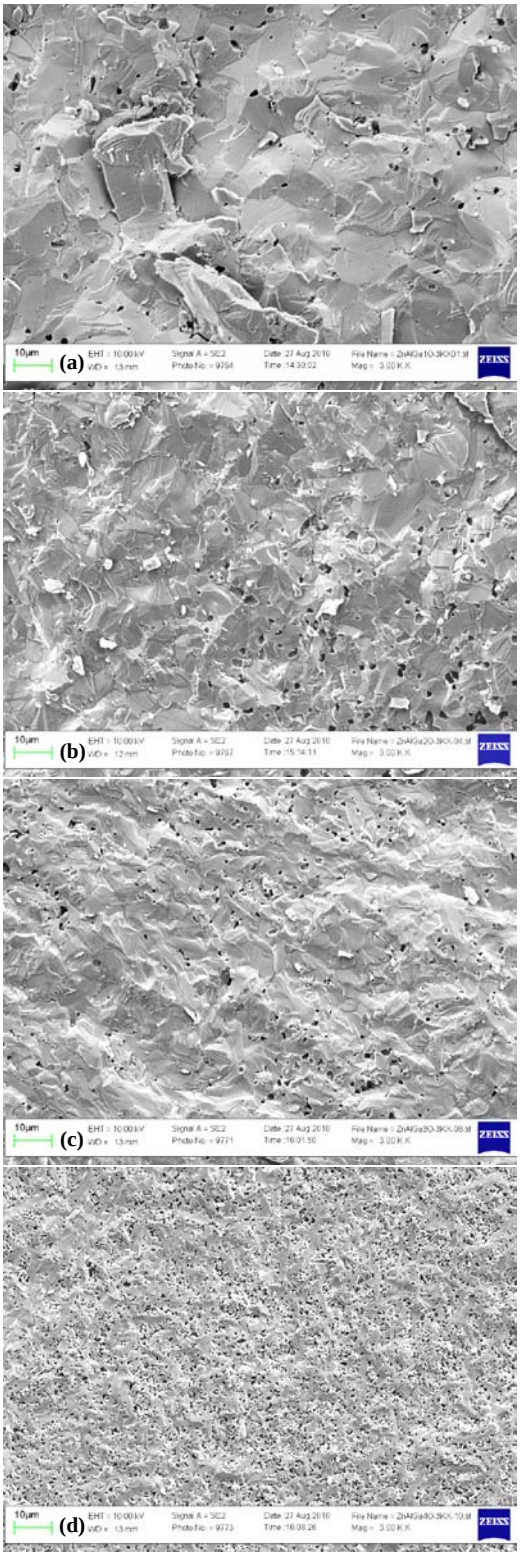

Fig.2 SEM images of Al- and Ga-doped ZnO: (a) ZnAlGa1O (b) ZnAlGa2O (c) ZnAlGa3O (d) ZnAlGa4O

Figure 3 shows the electrical conductivity-temperature curves of the prepared samples. In the investigated temperature range, the electrical conductivity decreases with

increasing the temperature for all the samples, which indicates a metallic behavior [9]. It is noted that, at a fixed measuring temperature, the electrical conductivity decreases with increasing the content of Ga, except the very close values of ZnAlGa1O and ZnAlGa2O at high temperatures. The lower electrical conductivies in higher Ga-containing samples might be due to the existed Ga-containing impurity, as detected from Figure 1. In addition, the increase of the porosity could also be a contribution to the decrease in the electrical conductivity. However, the electrical conductivity of ZnAlGa3O measured in this work is about twice large compared to that with the same composition reported by Ohtaki et al [7], which was in the range of 631 to 316 S/cm from the room temperature to 1273 K.

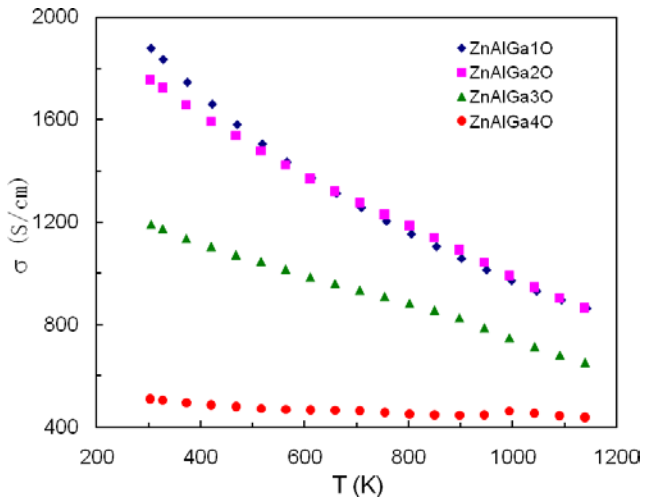

Fig. 3 Variations of electrical conductivity with temperature of the prepared samples

Figure 4 shows the variations of Seebeck coefficient with temperature of the prepared samples. It is noted that all the investigated materials show n-type behavior. The absolute value of the Seebeck coefficient increases with increasing the temperature for each sample. It is also noted that the effect of Ga content on the Seebeck coefficient is less remarkable than on the electrical conductivity. The Seebeck coefficient measured in this work is much smaller than the sample with the same composition reported by Ohtaki et al [7], which was ranging from -150 to -250 μV/K from the room temperature to 1273 K.

Figure 5 shows the variations of power factor with temperature of the prepared samples. The power factor increases with increasing the temperature and decreasing the Ga content, except the very close values of ZnAlGa2O and ZnAlGa3O. The effects of temperature and Ga content on power factor are their combining influences on the electrical conductivity and the Seebeck coefficient. The power factors obtained from this work are smaller compared to those reported by Ohtaki et al [7]. This is mainly attributed to the much lower Seebeck coefficient obtained in the present work, though the lower Ga-containing sample has larger electrical conductivity.

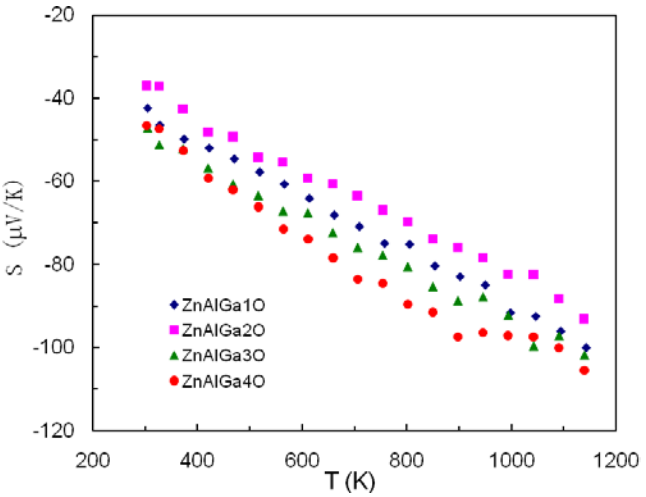

Fig. 4 Variations of Seebeck coefficient with temperature of the prepared samples

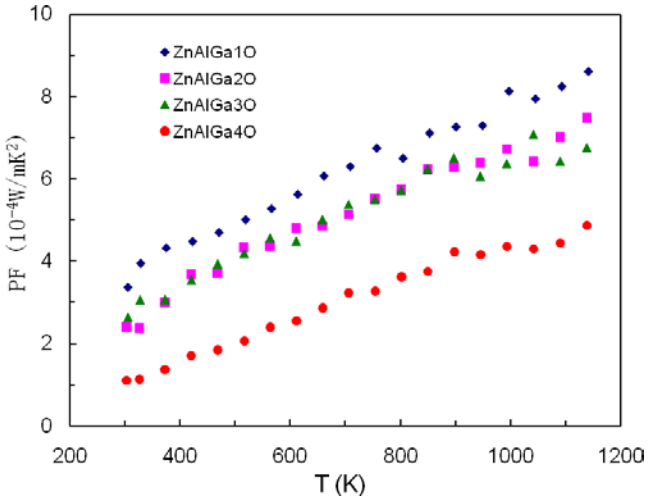

Fig. 5 Variations of power factor with temperature of the prepared samples

The thermal conductivity-temperature curves of the prepared samples are shown in Figure 6. For the samples of ZnAlGa1O, ZnAlGa2O and ZnAlGa3O, the thermal conductivity decreases with increasing the temperature. ZnAlGa4O shows the same behavior at low temperatures, then its thermal conductivity increases somehow with increasing the temperature from about 1000 K. The decrease in thermal conductivity with temperature could be attributed to the enhancement of phonon scattering as the temperature increases. The increase in thermal conductivity with temperature was predominated by intrinsic conduction, which is only for ZnAlGa4O. At a fixed measuring temperature, the thermal conductivity decreases with increasing the Ga content. From the Wiedemann-Franz's law, the contribution from the charge carrier to the total thermal conductivity is around 25 to 30% for the investigated samples. Therefore, the effect of Ga content on the electrical conductivity could be applied to

partially explain the effect of Ga content on the thermal conductivity. On the other hand, the results of density and microstructure caused by adding different contents of Ga could be used to describe its effect on the lattice contribution to the total thermal conductivity. In short, lower density (or higher porosity) and smaller grain size lead to lower thermal conductivity. It is noted that the thermal conductivity measured in this work is comparable to the sample with the same composition reported by Ohtaki et al [7], which was in the range of 13 to 5 W/mK from the room temperature to 1273 K.

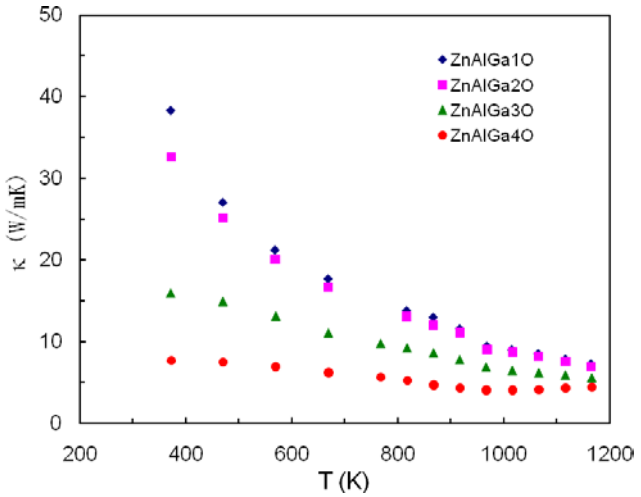

Fig. 6 Variations of thermal conductivity with temperature of the prepared samples

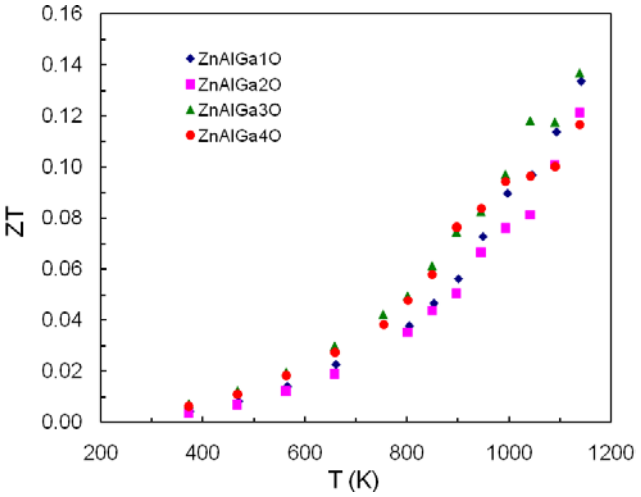

Fig. 7 Variations of dimensionless figure of merit with temperature of the prepared samples

Figure 7 shows the variations of dimensionless figure of merit, ZT, with temperature for the different samples. For all the investigated samples, the ZT increases with increasing the temperature. A ZT range of 0.12 to 0.14 was obtained at 1140 K for the investigated samples, which is much smaller than that of 0.65 at 1247 K reported by Ohtaki et al [7]. However, it should be noted that the electrical conductivities of our ZnAlGa1O, ZnAlGa2O and ZnAlGa3O samples are much larger than the referred samples suggesting a higher carrier concentration in our materials. The higher carrier concentration is generally giving a lower Seebeck coefficient. To confirm this point, Hall-effect measurements need to be done further. Although the ZT was not improved compared to the previous report, this work has pointed out that the thermoelectric performance of Al-doped ZnO is very sensitive to the second doping element, particularly with Ga. In addition, though the nominal compositions between our work and the refered work [7] are same, the actual compositions, which are strongly depending on the materials processing at different departments, might be different. On the other hand, thermoelectric properties are also depending on the measurement conditions. Further work will focus on turning the content of Al to approach the reported real composition showing excellent performance.

IV. Conclusions

For the investigated samples of dually Al- and Ga-doped ZnO, the electrical conductivity and the thermal conductivity at fix temperatures decrease with increasing the content of Ga, while the Seebeck coefficient was observed to be less influenced by the Ga content. A ZT range of 0.12 to 0.14 was obtained at 1140 K for the investigated samples, which is much smaller than that of the state-of-the-art. This is mainly attributed to the much lower Seebeck coefficient obtained in the present work, though the electrical conductivity is higher and the thermal conductivity is comparable.

Acknowledgment

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