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EFFECT OF 0.5 AT.% INDIUM ADDITION ON THERMOELECTRIC PROPERTIES OF GALLIUM DOPED-ZINC OXIDE BULK[#]

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Abstract. Thermoelectrics (TE) is well-known as a non-smoke technology for electricity production from waste heat and for greenhouse effect reduction. Enhancing power factor (PF = $S^2\sigma$, where S is Seebeck coefficient and σ is electrical conductivity) and figure of merit of TE materials to achieve high-performance TE devices has attracted much scientific attention. Doping foreign elements into host bulk structure is a basic and traditional solution to modify the thermoelectric properties of materials. In this work, we use small amount of 0.5 at.% In as dopant which is incorporated into Ga-doped ZnO (GZO) bulk by using solid-state reaction method. The effects of In addition on electrical and thermoelectric characteristics of the GZO bulk are discussed in detail. As a result, the electrical conductivity of the In and Ga co-doped ZnO (IGZO) bulk increases more than 20 % as compared to the GZO bulk. The Seebeck coefficient decreases insignificantly, which leads to enhancing power factor by 55 % from 184.4 $\mu W/mK^2$ (GZO) to 285.2 $\mu W/mK^2$ (IGZO) at 500 ^oC. The results open possibility to enhance the figure of merit of pure and doped ZnO material.

Keywords: thermoelectric materials, Ga-doped ZnO bulk, In addition, power factor.

Classification numbers: 2.8.2, 2.9.2, 3.4.1.

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1. INTRODUCTION

Nowadays, demand for energy increases quickly with increasing global population. Almost energy sources come from the fossil fuels such as petroleum, coal, natural gas, etc. These sources affect seriously to environment and people's health. Besides, many researches show that only 34 % of energy from the fossil fuels has been used, the remain has been energy loss and waste heat [1]. It not only wastes the energy, but also decreases the working efficiency of devices, engines, transportation, and so on. Consequently, it is essential to figure out a solution for limiting and recovering the amount of waste heat.

Thermoelectric (TE) materials emerge as a potential solution for the above challenge. It is much attracted by scientists and companies around the world, which is expressed through the number increase of thermoelectric-related annual publications from about 500 (in 1996) up to about 3000 (in 2016) [2]. According to the Seebeck phenomenon, TE materials-based devices can harvest and convert heat to electricity, which is known as a TE power generator (TEG). In contrast to the TEG, a TE cooler (TEC) is formed which is based on the Peltier effect.

Among the TE materials, there has been many reports on pure and doped ZnO materials [3 – 6]. Thanks to safety, cheapness and ability of easy controls in electrical conductivity by dopants, ZnO-based materials show significant improvement in thermoelectric properties, especially at high temperature. However, poor thermal stability as well as lifetime of ZnO-based TE devices limit their applications. In this study, therefore, we consider adding a tiny amount of In into Ga-doped ZnO (GZO) bulk, which is expected to enhance thermoelectric power factor of the In and Ga co-doped ZnO (IGZO) bulk. Furthermore, the combination of In and Ga dopants was indicated to increase the thermal stability of the ZnO materials [7].

2. MATERIALS AND METHODS

The method chosen to fabricate ZnO-based bulks was traditional solid-state reaction. The compositions were fixed at Zn : Ga = 95 : 5 at.% for the GZO bulk, and Zn : Ga : In = 95 : 4.5 : 0.5 at.% for the IGZO bulk. The component powders were ZnO (99.9 %, Merck, Germany), Ga_2O_3 (99.99 %, Sigma Aldrich, US) and In_2O_3 (99.99 %, Sigma Aldrich, US), which were wet ball-milled for 5 hours. After that, the powder mixture was compacted by using a hydraulic compressor, then was sintered at 1350 ^oC for 24 hours in total.

The crystalline structure of the as-sintered IGZO bulk was compared to that of the GZO bulk by using an X-ray diffraction system (XRD, Bruker D8 Advanced, Japan). To estimate the TE power factor, it is necessary to determine electrical conductivity and Seebeck coefficient of the bulks, which was carried out on a thermoelectric system (Ulvac-Riko ZEM-3, Japan).

3. RESULTS AND DISCUSSION

The XRD spectra taken to investigate the crystalline structure of the GZO and IGZO bulks are in Figure 1. Both samples have wurtzite-structural characteristics of the host ZnO material, such as (100), (002), (101), (110), etc. oriented planes (JCPDS 36-1451). Besides, it is seen that some peaks belonging to the inhomogeneous $Zn_9Ga_2O_{12}$ phase appear (JCPDS 50-0448). Almost XRD intensity peak of the ZnO phase in the IGZO bulk tends to increase, as compared to the GZO bulk. Normally, the increase of XRD intensity can give rise to increasing number and quality of crystals [8]. To estimate the crystal quality, however, it is also necessary to consider

the full width at half maximum (FWHM) value of the XRD peaks, which is responsible for mean crystal size along a certain orientation. The mean crystal size (D) along the main orientations, e.g. (100), (002) and (101) of the GZO and IGZO bulks were calculated from the Scherrer formula and shown in Table 1.

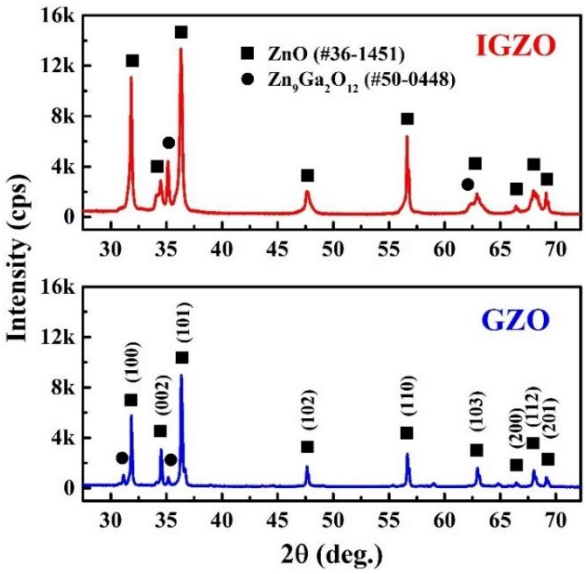

Figure 1. XRD patterns of the GZO and IGZO bulks.

Table 1. Crystallographic information of the GZO and IGZO bulks.

Samples	Orientations	2θ (deg.)	FWHM (deg.)	D (nm)
GZO	(100)	31.86	0.1519	54.4
	(002)	34.53	0.1772	46.9
	(101)	36.36	0.1790	46.7
IGZO	(100)	31.82	0.1669	49.5
	(002)	34.49	0.5145	16.2
	(101)	36.30	0.2503	33.4

As seen in Table 1, all the mean crystal sizes along (100), (002) and (101) planes of the IGZO bulk are correspondingly smaller than those of the GZO sample. Due to the larger ionic radius of In^{3+} (0.81 Å) than Zn^{2+} (0.74 Å) and Ga^{3+} (0.62 Å) [9], the possibility of Zn^{2+} substitution by In^{3+} is lower than that by Ga^{3+}. Thus, the In^{3+} may exist mainly at interstitial sites, which increases the number of crystals but decreases the crystal size. Another reason that can restrict the crystal size is the formation of $Zn_9Ga_2O_{12}$ in the IGZO sample. In fact, the $Zn_9Ga_2O_{12}$ phase appear in the GZO bulk, but increases strongly and inhibits the ZnO (002) peak in the IGZO sample. However, mechanism of In enhancing the $Zn_9Ga_2O_{12}$ has not been clarified.

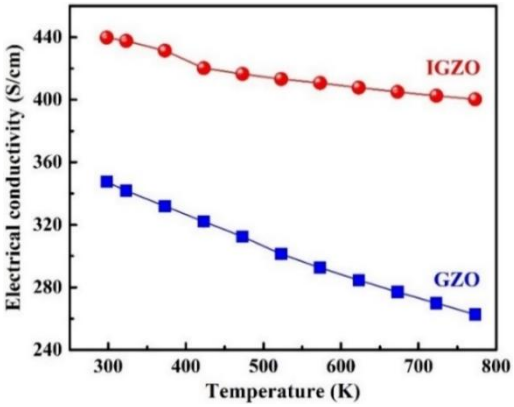

Figure 2. Electrical conductivity of the GZO and IGZO bulks as a function of temperature.

Figure 2 illustrates the variation of electrical conductivity versus temperature of the GZO and IGZO bulks. It is seen that the IGZO bulk has higher value of electrical conductivity than the GZO sample. It can be attributed to additional free-electron contribution of In^{3+} at the substitutional and interstitial sites. Besides, the electrical conductivities of both samples tend to reduce with increasing temperature. It is explained in term of the reduction of electron density, especially at high temperature [7, 10]. With increasing temperature, the Ga^{3+} and In^{3+} can remove from the Zn^{2+} substitutional sites to the interstitial sites, which is easy to be oxidized to form oxides and inhomogeneous compounds. It leads to decreasing the electron density of the bulks. Furthermore, the result also indicates that the IGZO bulk has better thermal stability than the GZO sample, which was suggested in the reference [7]. As a result, at 773 K, the electrical conductivity of the IGZO bulk (400.3 S/cm) is higher than that of the GZO sample (262.7 S/cm).

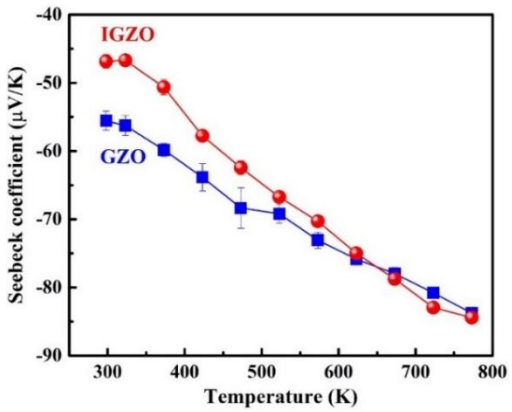

Figure 3. Seebeck coefficient of the GZO and IGZO bulks as a function of temperature.

Figure 3 shows the temperature-dependent Seebeck coefficient of the GZO and IGZO bulks. All the values are negative, which suggests the n-type conduction characteristics with electrons as major carriers. At room temperature, the IGZO bulk has lower absolute value of Seebeck coefficient than the GZO bulk. As mentioned above, the electron density of the IGZO bulk can be higher than that of the GZO sample due to In^{3+} donors. It results in lower Seebeck coefficient for the IGZO bulks due to the inverse proportion with electron density, which is expressed in the Pisarenko relation as follows [11]:

$$S = \frac{8\pi^2 k_B^2 T}{3qh^2} m^* \left(\frac{\pi}{3n}\right)^{2/3}$$

where S is the Seebeck coefficient; T is absolute temperature; m^* is effective mass of electron; n is the electron density; q, k_B and h are the elementary charge, Boltzmann and Planck constants, respectively.

Besides, the absolute values of Seebeck coefficient of both samples tend to increase with increasing temperature. It can also be assigned to the reduction of electron density, which is in agreement with the reduction of eletrical conductivity versus temperature, as discussed above. The Seebeck coefficient obtains the highest value of ~84 μV/K at 773 K for the GZO and IGZO bulks.

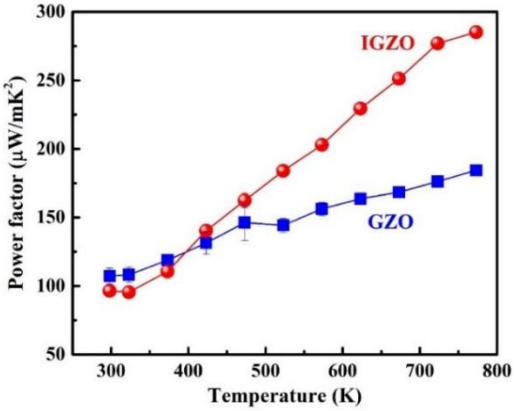

Figure 4. Thermoelectric power factor of the GZO and IGZO bulks as a function of temperature.

Figure 4 displays the evolution of power factor of the GZO and IGZO bulks versus temperature. The power factor (PF) is calculated by $PF = S^2\sigma$, where S is the Seebeck coefficient and σ is the electrical conductivity. The PF characterizes for ability to produce large or small voltage of thermoelectric materials and devices, which is indicated equivalently as important as the thermoelectric conversion efficiency [12]. Despite not much difference in Seebeck coefficient, the much higher electrical conductivity leads to enhancing significantly power factor of the IGZO bulk (285.2 μW/mK^2) in comparison with that of the GZO bulk (184.4 μW/mK^2).

4. CONCLUSIONS

In this study, the effect of 0.5 at.% In on thermoelectric properties of Ga-doped ZnO bulks fabricated by solid-state reaction method is investigated. The XRD analysis shows the development of inhomogeneous $Zn_9Ga_2O_{12}$ phase in the IGZO bulks. The In addition into the GZO bulks increases strongly the electrical conductivity while the Seebeck coefficient decreases insignificantly. It suggests their dependence on the reduction of electron density versus temperature. As a result, the power factor of the IGZO bulk (285.2 μW/mK^2) is much higher than that of the GZO bulk (184.4 μW/mK^2). The relationship between the inhomogeneous phase and electron density will be considered in following works.

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