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The improvement of thermoelectric property of bulk ZnO via ZnS addition: Influence of intrinsic defects

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ABSTRACT

As in any semiconducting solids, intrinsic defects can affect the properties of ZnO, such as the electrical and thermal conductivities. Defect engineering is usually focused on optimizing the materials' synthesis or annealing parameters, i.e., temperature, atmosphere, etc. Here we report an approach to change the intrinsic defects of ZnO by adding a small amount of ZnS. During the sintering process, ZnS was decomposed. Apart from the formation of SO₂, the decomposed S and Zn can also be simultaneously doped onto O and Zn sites to change the intrinsic defects in ZnO. For instance, some of the S was converted to SO₂ and led to the formation of V_O (oxygen vacancy); meanwhile, Zn may move to the V_{Zn} (Zn vacancy) site and decrease the concentration of Zn vacancy. Due to the changes in these native defects, the carrier concentration increased and the thermal conductivity decreased when the content of ZnS was increased to x = 0.01. This sample had an optimal zT value, which was twice that of undoped ZnO. However, with further increase in ZnS, the carrier concentration was reduced. These results suggest a method to tune the intrinsic defects of ZnO via doping technology and bring potential opportunities to improve the thermoelectric performance of this oxide.

1. Introduction

There has been an increasing interest in the field of materials for thermoelectric (TE) energy conversion as this technology can be used to reduce our reliance on fossil fuel [1]. This environment-friendly technology harvests energy through the recovery of waste heat and converts it into useful electricity [1]. High-temperature waste heat is abundant in industrial processes, including petroleum production, steel manufacturing, and transportation. Therefore, materials that are stable at high temperatures are required to construct waste heat recovery systems using thermoelectric technology. Because of the inherent merit, i.e., tolerance of large temperature gradients, oxides are promising candidates.

ZnO with wurtzite structure is being studied for use as an n-type thermoelectric material [2]. The intrinsic defects in ZnO have been investigated both theoretically [3] and experimentally [4]. Oxygen or zinc vacancies (V_O, V_{Zn}) and oxygen or zinc interstitials (O_i, Zn_i) are responsible for its electrical conductivity [5]. Different sintering atmosphere and sintering methods have been used for defect engineering

in ZnO, thus tuning the thermoelectric performance of this oxide [6,7]. For example, a reducing sintering atmosphere was found to decrease the intrinsic acceptor defects such as V_{Zn} and O_i in ZnO. As a result, the charge carrier concentration was increased and improved electrical conductivity and zT were obtained [6].

Besides engineering intrinsic defects, doping technology is another way to improve the TE property of ZnO. It has been found that the TE performance of ZnO can be improved by cationic substitutions with Al [8–10], Ga [11], In [12], Sc [13], Ti [14], Sb [15], Co [16], etc. Anion substituted ZnO has also been widely studied, but most of them are for optoelectronic devices. For example, photoconductivity of ZnO films was enhanced by co-doping with Te and N [17].

Thermoelectric performance of bulk ZnO_{1–y}S_y (y = 0, 0.01, 0.03, 0.05) was previously reported [18]. The samples were synthesized using ball milling ZnO and ZnS powders, followed by sintering under Ar atmosphere. It was found that the power factor (PF) was improved [18], which may be attributed to the decreased band gap after S doping [19–21]. However, thermal conductivity was not measured in their study to determine the zT performance.

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In the present work, bulk $(1-x)\text{ZnO}-x\text{ZnS}$ ($x = 0, 0.01, 0.03$ and 0.05) samples were prepared to perform a systematic evaluation of the thermoelectric properties, including electrical conductivity, thermopower, and thermal conductivity. It was found that under air sintering atmosphere, ZnS was decomposed and reacted with oxygen to form SO_2 . Besides the formation of SO_2 , the rest of the S and Zn may go to O and Zn sites respectively. The native defects in ZnO were influenced accordingly, and thus thermoelectric performance was affected. Similar intrinsic defects introduction by doping was studied in 2D transition metal dichalcogenide (TMD) TiSe_2 , and high-spin-polarized current and local magnetic moment were obtained [22]. It is anticipated that by optimizing defects via doping will be a useful approach to improve thermoelectric or other intrinsic physical properties of materials.

2. Experimental procedure

ZnO-based ceramics were produced by the solid-state reaction of mixtures of high purity ZnO and ZnS powders (Sigma Aldrich > 99.9%) for the purpose of studying their thermoelectric-related behavior. Four samples were produced in the following powder ratios: $(1-x)\text{ZnO}-x\text{ZnS}$, where $x = 0, 0.01, 0.03$ and 0.05 . The powder mixtures were first ball milled for 8 h; the resulting powders were mixed with a small amount of polyvinyl alcohol binder dissolved in water and pressed into pellets. The binder was then removed by heating the samples in the range from 473 to 623 K. Subsequently, the pellets were sintered at 1673 K for 5 h in the air. The decomposition in the air was also measured using thermogravimetry (TG) (SDT TA Instrument Q600).

The structures of the sintered samples were studied using a variety of techniques. Phase characterization was carried out by X-ray diffraction (Bruker D8) using $\text{Cu K}\alpha$ radiation. Rietveld refinement of the resulting XRD traces was performed using TOPAS software. Microstructural analysis was carried out using a field-emission scanning electron microscope (JEOL JSM-6340F) on the sample surfaces which had been polished and then thermally etched.

Additionally, reflectance spectra were obtained using a UV–Vis spectrophotometer (PerkinElmer Lambda 950) with an integrating sphere. Reflectance was then converted to absorption coefficient using the Kubelka-Munk relation [23] and the resulting band gap energy was calculated according to the Tauc equation [24]. Photoluminescence (PL) spectra were obtained using a Cary Eclipse Spectrofluorophotometer with a Xe pulse lamp. The measurements were carried out on each sample at room temperature under identical conditions after the samples were excited at 325 nm.

The electronic and thermoelectric characteristics were measured as follows: carrier concentration and mobility were measured using a Hall measurement system (Bio-Rad HL5500). Electrical resistivity and thermopower were measured, as a function of temperature, from room temperature to 973 K, using a Seebeck probe system (ULVAC-RIKO ZEM-3, Japan). Thermal conductivity (κ) was obtained from thermal diffusivity (D), specific heat (C_p) and density (d) using the relation $\kappa(T) = D(T) \times C_p(T) \times d$. $D(T)$ was measured using a laser flash apparatus (NETZSCH LFA 457). $C_p(T)$ was measured on a Thermogravimetric Analyzer (TA 2950) and d was measured at room temperature by Archimedes method.

3. Results and discussions

Fig. 1 shows the room-temperature XRD patterns of the as-synthesized (sintered) samples. All the diffraction peaks can be indexed to the wurtzite structure of ZnO (space group $P6_3mc$, PDF# 04-005-5076).

Electrical resistivity and thermopower of $(1-x)\text{ZnO}-x\text{ZnS}$ samples, as a function of temperature, are shown in Fig. 2(a) and (b). With increasing content of ZnS, the electrical resistivity was first decreased. The lowest electrical resistivity was observed in the sample with $x = 0.01$, and the values were 2 times and more than an order of magnitude lower than those of the undoped counterpart, at 973 K and 300 K

Fig. 1. XRD patterns of $(1-x)\text{ZnO}-x\text{ZnS}$ samples.

respectively. All the samples exhibited mixed conduction characteristics. This phenomenon has also been reported in Co-doped ZnO [16], Sc-doped ZnO [13] and undoped ZnO thin films [5]. According to the negative values of thermopower (Fig. 2(b)), all the samples are n-type. While the electrical resistivity decreased with increasing temperature from 300 K to 973 K, the absolute values of thermopower did not follow the trend (Fig. 2(a) and (b)). This suggests that the decrease in electrical resistivity in this temperature range (300 K–973 K) was not simply attributed to the increased charge carrier concentration. The electrical resistivity and the absolute values of thermopower at 300 K, as a function of ZnS level, are shown in Fig. 2(c). The minimum value was observed in the sample with $x = 0.01$ in both electrical resistivity and the absolute value of thermopower.

All the as-prepared samples have high relative densities (~91% to 94%), as evidenced by the SEM image in Fig. 3. Therefore, it can be concluded that the variation in electrical properties of the samples was not closely related to their densities. In order to understand the mechanism of the electrical transport behavior in this system, Hall Effect measurements were conducted at room temperature, and the results are presented in Fig. 4. It is found that room temperature electrical resistivity of the undoped ZnO in this study was lower than that of nanostructured bulk ZnO [12] but higher than that of ZnO thin film [5], probably due to the different charge carrier concentration related to the difference in the synthesis process. The change in charge carrier concentration was more than 4 times (sample $x = 0.01$), whereas the mobility was changed by less than 10%. This indicates that the electrical resistivity and thermopower were predominantly dependent on the charge carrier concentration (Fig. 2(c)). The decreased electrical resistivity in the sample with $x = 0.01$ (Fig. 2(c)) could be ascribed to the increased carrier concentration (Fig. 4), although the Hall mobility was slightly decreased (Fig. 4) which could be due to the scattering from increased carriers. The change in carrier concentration could not be simply explained in terms of band gap energy in this system since all the doped samples had slightly higher band gap energies than ZnO (Fig. S1 and Table S1).

The semiconducting behavior of ZnO is closely related to the deviation from stoichiometry due to the presence of intrinsic defects, such as oxygen and zinc vacancies (V_o , V_{zn}) [5]. ZnS in this work changed those intrinsic defects of ZnO. During the sintering process, ZnS was decomposed and reacted with oxygen through the following equation:

This was confirmed by the weight loss in TG results (Fig. S2). Besides the formation of SO_2 , the rest of the S and Zn would go to ZnO.

In the sample with $x = 0.01$, Zn could fill in V_{zn} , which led to the

Fig. 2. Temperature dependence of (a) electrical resistivity and (b) thermopower of (1-x)ZnO-xZnS samples. (c) Electrical resistivity and the absolute value of thermopower of (1-x)ZnO-xZnS as a function of ZnS content at 300 K.

Fig. 3. Representative SEM micrograph of the polished and thermally-etched undoped ZnO.

increase in the carrier concentration. Meanwhile, the formation of SO_2 would produce V_o , resulting in an increase in carrier concentration as well. Similar “dual-native-defects” engineering was introduced in 2D transition metal dichalcogenide (TMD) TiSe_2 in order to achieve a high-spin-polarized current and local magnetic moment [22]. As the concentration of ZnS was raised above $x = 0.01$ ($x = 0.03$ and $x = 0.05$), besides the formation of SO_2 , the rest of S could fill in V_o . The former increased the charge carrier concentration while the latter would compensate part of the increased charge carrier concentration, and eventually leading to the decreased charge carrier concentration in the

Fig. 4. Carrier concentration (n), Hall mobility (μ) and electrical resistivity (ρ) of (1-x) ZnO-xZnS samples.

Table 1

Carrier concentration (n) and Hall mobility (μ) of ZnO, $x = 0.01$ sample and singly-doped samples: 0.99ZnO-0.01Zn, 0.99ZnO-0.01S and 0.97ZnO-0.03S.

Sample	μ ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	n (10^{17}cm^{-3})
$x = 0$ (ZnO)	49.6	2.5
0.99ZnO-0.01Zn	3.3	4.1
0.99ZnO-0.01S	35.4	6
0.97ZnO-0.03S	4.4	2.4
$x = 0.01$	45.9	8.2

Fig. 5. Room temperature PL spectra of (1-x)ZnO-xZnS samples.**Table 2**

Atomic coordinates, equivalent isotropic thermal parameters B ($\text{\AA}^2$), and position occupancies (Occ.) in (1-x)ZnO-xZnS samples derived from Rietveld analysis.

Composition	$x = 0$	$x = 0.01$	$x = 0.03$	$x = 0.05$
Lattice parameter ($\text{\AA}$)				
a	3.2510	3.2509	3.2512	3.2507
c	5.2077	5.2070	5.2077	5.2070
Zn				
x	0.3333	0.3333	0.3333	0.3333
y	0.6667	0.6667	0.6667	0.6667
z	0.0000	0.0000	0.0000	0.0000
$B(\text{\AA}^2)$	0.31	0.31	0.31	0.31
Occ.	0.9346	1.0000	1.0000	0.9999
O				
x	0.3333	0.3333	0.3333	0.3333
y	0.6667	0.6667	0.6667	0.6667
z	0.3807	0.3886	0.3810	0.3823
$B(\text{\AA}^2)$	0.55	0.55	0.55	0.55
Occ.				
O	0.9989	0.9541	0.9778	0.9112
S	-	0.0013	0.0054	0.0014
R_{exp}	2.69	2.64	2.61	2.63
R_{wp}	7.98	7.83	7.81	7.94
R_p	6.00	5.90	6.00	6.26
GOF	2.97	2.97	2.99	3.02

sample with $x = 0.03$, as compared with the value in the sample with $x = 0.01$ (Fig. 4). It was reported that when the charge carrier concentration exceeded a certain limit in Al-doped ZnO, the energy to form “electron killer” defects would be reduced and resulted in more charge carriers being compensated [25,26].

In order to support the above hypothesis and to elucidate the influence of local defects on the electron transport properties of this system, Hall Effect measurements at room temperature were conducted on the singly-doped samples, i.e., 1% Zn, 1% S and 3% S doped ZnO. They are named as 0.99ZnO-0.01Zn, 0.99ZnO-0.01S and 0.97ZnO-0.03S respectively and were prepared in the same way as described before. XRD results confirmed that all the samples had single phase ZnO

Fig. 6. Temperature dependence of power factor (PF) of (1-x)ZnO-xZnS samples. **Fig. 7.** Temperature dependence of thermal conductivity of (1-x)ZnO-xZnS samples. **Fig. 8.** Temperature dependence of zT values of (1-x)ZnO-xZnS samples.

(Fig. S3). The Hall Effect measurement results are listed in Table 1.

Compared with ZnO, the carrier concentration of 0.99ZnO-0.01Zn was higher. This is because the filling of Zn in V_{Zn} would produce more charge carriers. The 0.99ZnO-0.01S sample had higher carrier concentration as well, which could be attributed to the V_o formation due to the oxidation of S. Therefore, the charge carrier concentration of the

“single doped” samples can explain the increased carrier concentration in the sample with $x = 0.01$. In this case, Zn suppressed the “electron killer” V_{Zn} and the formation of SO_2 would produce V_{O} , both of which increased the carrier concentration (Fig. 4). Compared with 0.99ZnO-0.01S, 0.97ZnO-0.03S has lower carrier concentration, mainly because the rest of S filled in V_{O} , compensating part of the increased charge carrier concentration from V_{O} produced due to the formation of SO_2 .

Photoluminescence (PL) spectroscopy is a non-destructive method of observing defects in ZnO [4,27–29]. The PL spectra of the studied samples are shown in Fig. 5. The visible emission in Fig. 5 resulted from energy levels of intrinsic defects lying within the band gaps of ZnO [4,27–29]. It is observed that the PL intensities changed when x increased. For example, PL intensities of samples with $x = 0.01$ and $x = 0.03$ were weaker than that of undoped ZnO, which indicates that the defects in those samples were suppressed after the introduction of ZnS.

In order to clarify the defects in ZnO, site occupation was calculated via the XRPD Rietveld analysis. The observed, calculated and difference profiles are shown in the Supplementary material, Fig. S4. The Rietveld refinement results were listed in Table 2. It was found that the undoped ZnO has the lowest Zn occupancy. It was reported that high concentration of zinc vacancies was obtained in oxygen-annealed CVT-grown ZnO crystals [30]. The decreased PL intensities in $x = 0.01$ and $x = 0.03$ could be mainly attributed to the decreased V_{Zn} or increased Zn occupancy (Table 2) in these two samples. As x increased from $x = 0.01$ to $x = 0.03$, more S filled in V_{O} , leading to the decreased charge carrier concentration (Fig. 4). In the sample with $x = 0.05$, O occupancy was the lowest. S_i (S interstitial) or a defect cluster with S and O could be formed, which resulted in the highest defects among the studied samples (Fig. 5). These defects compensated each other, resulting in decreased charge carrier concentration in the sample with $x = 0.05$ (Fig. 4). However, XRD didn't detect them (Fig. 1) due to its low concentration level.

Fig. 6 presents the temperature dependence of power factor (PF) for the synthesized samples. The power factor of ZnO was enhanced with the introduction of ZnS. The sample with $x = 0.01$ had an optimal value of $1.73 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$ at 973 K, which was higher than that of the undoped ZnO by around 80%. This is attributed to the almost constant μ and the increased n (Fig. 4), resulting in the lowest electrical resistivity in this sample (Fig. 2(a)). Further increase in x led to a decrease in PF.

Fig. 7 shows the thermal conductivity of the samples as a function of temperature. The thermal conductivity decreased with increasing temperature. The introduction of ZnS slightly decreased the thermal conductivity, especially at temperatures lower than 600 K. At 373 K, the sample with $x = 0.01$ had the lowest thermal conductivity, which was $\sim 20\%$ lower than that of its undoped counterpart. In the sample with $x = 0.01$, adding ZnS increased the carrier concentration (Fig. 4), which resulted in more electron-phonon scattering, thus decreasing the thermal conductivity.

Fig. 8 shows the zT value of the samples as a function of temperature. The zT values increased with increasing temperature. The highest zT of ~ 0.038 was observed at 973 K in the sample with $x = 0.01$, which was twice that of the undoped ZnO. The thermoelectric performance is comparable with those of reported doped ZnO bulk samples [10,16]. Further increase in x led to a decrease in zT , which was associated with the decrease in power factor (Fig. 6).

4. Conclusions

$(1-x)\text{ZnO}-x\text{ZnS}$ samples have been prepared through solid-state reaction in air. All the samples exhibited high relative densities ($\sim 91\%$ to 94%). Band gap was increased with increasing content of ZnS. The electrical resistivity and the absolute values of thermopower at 300 K as a function of ZnS level showed similar variation trends. An optimal power factor (PF) was obtained in the sample with $x = 0.01$. The

highest carrier concentration in this sample was due to the change of intrinsic defects by ZnS addition. Moreover, the incorporation of ZnS decreased the thermal conductivity by $\sim 20\%$. As a result, the zT value at 973 K in the sample with $x = 0.01$ was improved by 2 times as compared to that of the undoped ZnO.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.ceramint.2018.01.043>.

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