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Reprocessing Leading to Lower Thermal Conductivity of ZnO Thermoelectrics

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Abstract

Nanometer sized ZnO powder was co-doped with gamma aluminum oxide and gallium oxide and sintered using a direct current sintering furnace. Sintered samples were reprocessed by crushing the samples in a Carver press, then milling for 4 hours. The reprocessed samples were then re-sintered in the direct current sintering furnace. Heat capacity, density and thermal diffusivity were measured in order to determine thermal conductivity as a function of temperature. Thermoelectric properties were measured. It was found that the thermal conductivity decreased from 7 W/m K to 3.5 W/m K at 805K by using the reprocessing technique. It is projected that the value will be less than 2 W/m K and the figure of merit greater than 0.65 at 1400K.

Keywords: Thermoelectric; Oxide; Thermal Conductivity; Reprocessing; Direct Current Sintering

List of abbreviations: DCS: Direct Current Sintering; ZT: Figure of Merit; RTG: Radioisotope Thermoelectric Generator; ZnO: Zinc Oxide

Introduction

Oxide thermoelectric performance has shown steady increase in the past 25 years. There has been wide interest in applications such as waste heat recovery and radioisotope thermoelectric generators (RTG's) where potentially higher temperature use could lead to higher thermoelectric generator efficiency [1]. A higher use temperature will also yield a higher figure of merit (ZT). Zinc Oxide (ZnO) is a promising candidate as an n-type thermoelectric temperature due to its high temperature stability, non-toxic nature and low-cost [2]. ZnO is a wide direct gap semiconductor with high electron mobility and thermal conductivity [3]. ZnO has a high thermal conductivity which adversely effects thermoelectric performance. In one study, it was found that the room temperature value for Al-doped ZnO was 40 W/m K and 13 W/m K for dually doped (Al, Ga) ZnO [4]. The thermoelectric performance for Al-doped ZnO has been reported as a ZT=0.33 [5,6]. Nanostructuring has been used to improve thermoelectric efficiency in ZnO [7,8]. Using nanoparticles as the starting material, Al-doped ZnO had a thermal conductivity of ~2 W/m K at room temperature and a projected ZT ~ 0.44 at 1000K [7]. Introduction of nanovoids in the Al-doped ZnO samples resulted in a ZT ~0.6 at 1250 K [9,10]. However, there were difficulties in producing consistent homogeneity in the samples. Dually doping with aluminum and gallium resulted in a ZT=0.65 at 1247K [4]. Although the electrical conductivity decreased with the addition of gallium, the thermal conductivity of the sample was decreased to ~5 W/m K thus leading to the high value of ZT. It was also felt that nanostructuring also aided in the decrease in thermal conductivity. Spark plasma sintering (SPS) was used to densify dually-doped (Al, Ga) ZnO samples in another study [11]. Although, the thermal conductivity was decreased due to small grain sizes, the reported ZT of 0.14 was primarily due to a low power factor. It has been demonstrated that reprocessing thermoelectrics PbTe doped with 2 mol% Na and PbTe-SrTe (2 mol%) doped with 1 mol% Na in a SPS resulted in a higher ZT due to a reduced thermal conductivity [11]. This reduction in thermal conductivity was due to the formation of nanophases and mesophases in the materials which scattered a wider range of phonons.

In this study we used direct current sintering to densify co-doped Al, Ga ZnO samples and determine the thermal conductivity and thermoelectric figure of merit for singly processed and reprocessed material.

Materials and Methods

ZnO powders were purchased from American Elements. The average particle size was 18 nm which was measured using laser particle size analysis (Microtrac Bluewave). ϒ-Al_2O_3 and Ga_2O_3 (American Elements) were milled for 2 hours to 20 nm using a micromill with 0.2 mm ZrO2 milling media. The ϒ-Al_2O_3 and Ga_2O_3 were added to ZnO to obtain 50 grams of the composition, $Zn_{0.96}Al_{0.02}Ga_{0.02}O$. Then, 50 ml of methanol was added to the powder plus 1 cm diameter ZrO_2 balls (10 total) and the solution was mixed for six hours in a turbula (W.A. Bachhofen). The mixture was then allowed to dry overnight in a drying oven at 120C. This was repeated to give a total of 100 grams of material. The dried powder was then heated in a vacuum tube furnace at 850C for 6 hours at a vacuum of 1×10^{-4} Torr. Approximately 6 grams of powder was then placed in a graphite die and sintered at 850C for 5 minutes in a direct current sintering furnace (Thermal Technologies DCS 15-6) using 50 Mpa of applied pressure. The furnace profile consisted of heating at 100 C/min to 750C while increasing pressure at 10 Mpa/min to 35 Mpa. The furnace then stayed at this temperature and pressure for 2 minutes, and then the temperature was increased by 50C/min to 850C and 10 Mpa/min to 50 Mpa. The heating profile was such to prevent temperature overshoot at the maximum temperature. After soaking for 5 minutes, the temperature was decreased 100C/min to room temperature and the pressure was decreased by 50 Mpa/min to 5 Mpa. Sample density was measured using the Archimedes Method (Sartorius Practum). Specific heat was measured as a function of temperature to a maximum temperature of 900K using a DCS Q20 (TA Instruments). Thermal diffusivity was measured as a function of temperature to 900K using a Flashline X-Platform Model 350. Thermoelectric properties, Seebeck coefficient and resistivity were measured using a ZEM 3 furnace (ULVAC) to a maximum temperature of 840K. Seebeck samples were 2mm x 2mm x 20mm prepared using a diamond wire saw. Measurements were made at 50C intervals and three measurements were made at each temperature. The phase and microstructure of the samples were characterized using x-ray diffraction (XRD) and transmission electron microscopy (TEM). The XRD was performed in Phillips Diffractometer using Cu Kα (λCu=0.15141nm) as the source. The phases from the XRD scan were further confirmed by electron diffraction in an FEI Tecnai F20 scanning transmission electron microscope (STEM). The TEM sample was prepared by a focus ion beam (FIB) lift-out and annular milling procedure in FEI Quanta 3D dual beam FIB-SEM. Samples were also reprocessed by first crushing the samples in a Carver press, then milling the powder using 10, 1 cm diameter ZrO_2 milling media in a turbula for 4 hours. The sample was then re-sintered in the direct current sintering furnace.

Results

Figure 1 is an x-ray diffraction curve of the sintered material showing the presence of ZnO, but no phases involving ϒ-Al_2O_3 or Ga_2O_3. The curve labeled ZnO_03 is for the singly processed ZnO, while the curve labeled ZnO_02 is for the reprocessed sample. The lower curve is for the ZnO JCPDS file for comparison. Figure 1 shows a selected area diffraction pattern for the reprocessed sample, which confirms the x-ray diffraction results.

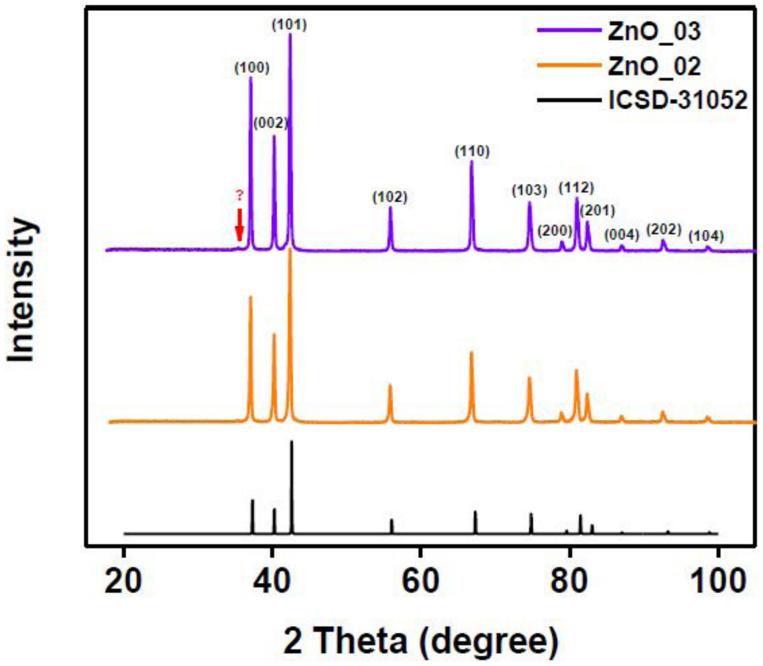

Figure 1: X-ray diffraction of singly processed (ZnO_0$_3$) and reprocessed dually doped ZnO (ZnO_0$_2$)

Density measurements yielded an average of 5.3 g/cc for the samples sintered once. For samples which were reprocessed this average dropped to 4.5 g/cc. Figure 2a and 2b is a scanning electron micrograph showing a representative example of each. The first micrograph shows a sample sintered once, while the second micrograph shows a reprocessed sample.

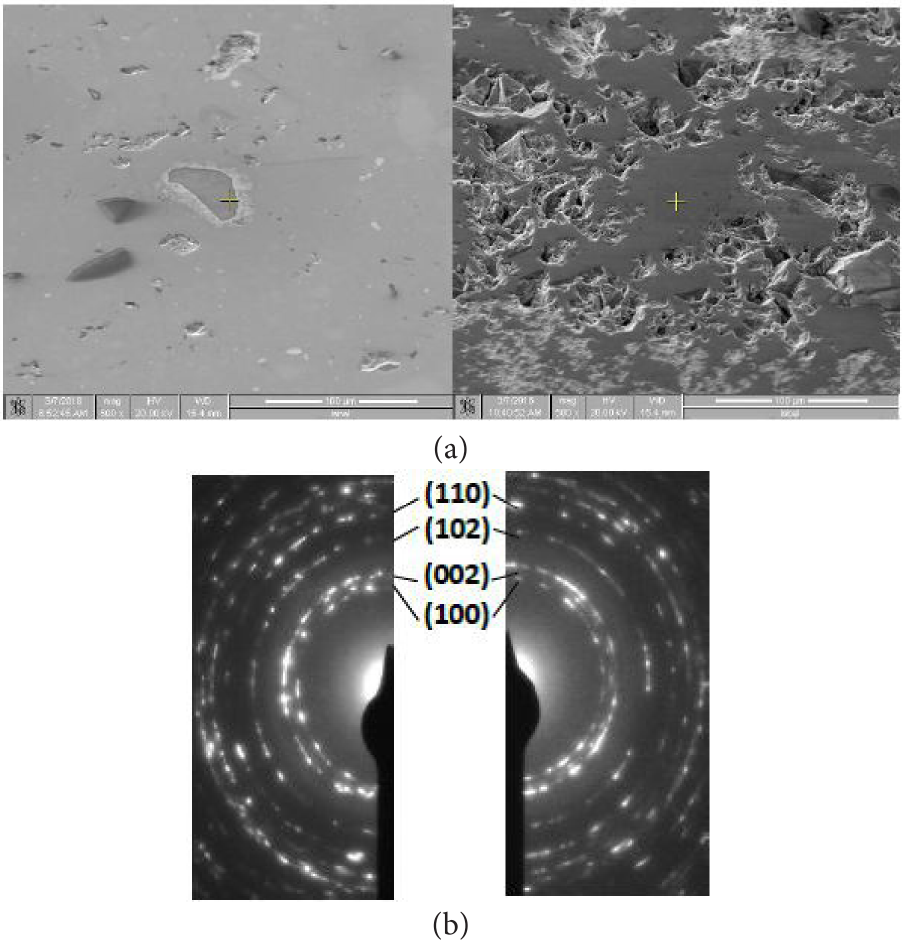

Figure 2: Scanning electron micrographs of co-doped ZnO sample sintered one time (left) and sample reprocessed (right)-Figure 2a and selected area diffraction patterns-Figure 2b

It can be seen from this figure that there is less porosity in the sample sintered once than in the reprocessed sample. There is also a more uniform grain size in the sample sintered once. One can identify a distribution of grain sizes in the sample which was reprocessed.

The thermal conductivity was calculated using $\kappa=\rho\alpha cp$.

For the singly processed samples the thermal conductivity at 904K was 7 W/m K while the reprocessed samples had a thermal conductivity of 3.5 W/m K. Figure 3 is a plot of thermal conductivity as a function of temperature for a reprocessed sample.

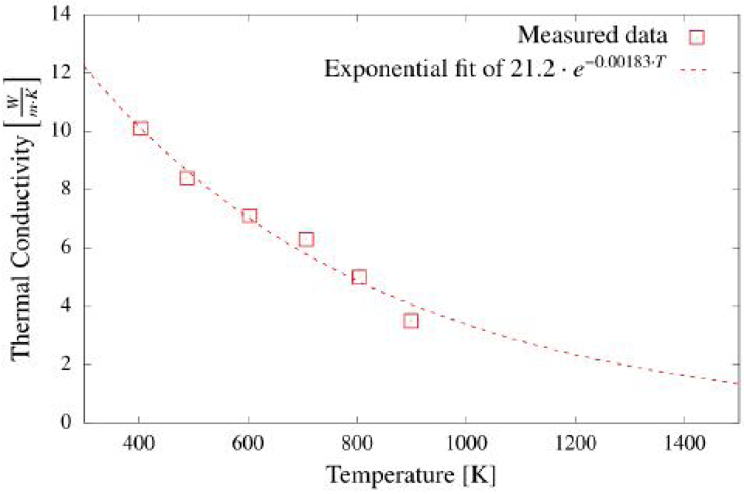

Figure 3: Plot of thermal conductivity versus temperature for a reprocessed co-doped ZnO sample

As seen from the figure, one can project a thermal conductivity of ~ 2 W/m K at 1400K.

A plot of power factor versus temperature is shown in figure 4. It can be seen that the power factor is quite low at 805K and increases steadily with a projection of almost 0.006 W/m K2 at 1400K.

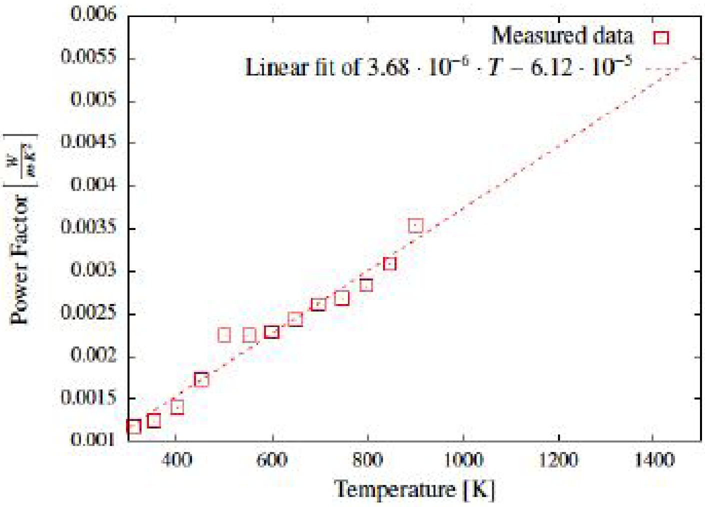

Figure 4: Plot of Power Factor versus Temperature

The figure of merit was calculated from ZT=σS2/κ.

Figure 5 is a plot of figure of merit ZT versus temperature for a reprocessed sample.

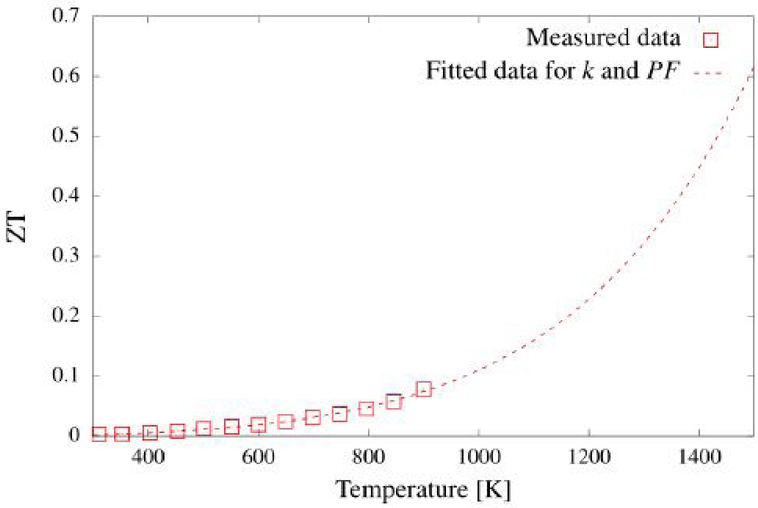

Figure 5: Figure of merit zT versus temperature for reprocessed sample

The figure of merit is only 0.1 at 904 K but is projected at 0.65 at 1400K.

Discussion

The decrease in thermal conductivity is most likely attributable to the lower observed density and a wider distribution of grain sizes due to reprocessing the material. The increased porosity and wider range of grain sizes would be able to scatter a wider spectrum of phonons than that of the higher density, uniform grained singly processed material. The lower than expected projected figure of merit for their processed material is due to the low power factor (0.00058 W/m K2) at 1400K. A power factor of an order of magnitude higher has been observed with the same atomic weight percent doping of aluminum and gallium. An order of magnitude increase for the power factor using the thermal conductivity data of this study would result in a figure of merit of greater than 1 at 1273K. Most likely, in this study, the aluminum and gallium atoms did not substitute fully in the ZnO crystal structure. The increased porosity would also lead to an increase in phonon scatter leading to a lower power factor. The samples were sintered in vacuum, which will induce oxygen vacancies, and electrons to preserve charge neutrality. Doping with aluminum and gallium should also increase electron charge carriers due to direct substitution with Zn. It has been observed that ZnAl2O4 phases form containing more than 1 mol% Al; however this was not observed in the x-ray diffraction spectrum in Figure 1 for this study [10]. It has also been observed that the addition of gallium extended the solubility limit of aluminum and should increase the likelihood of spinel formation, but again was not observed in the present study [10]. The calcination temperature of 1123K for 6 hours could be raised 200K to increase the probability of substitution and of the formation of the spinel structure. The sintering temperature, also 1123K can also be raised by as much as 200K to increase the likelihood of substitution and the formation of the spinel phase. Recently, it was shown that texturing Al-doped ZnO resulted in high power factors at 750K [12]. This technique involved sintering the powder in SPS, then placing the sintered bulk into a larger diameter die and sintering at a higher temperature and pressure resulting in a textured material. It is felt this technique would be useful for the co-doped materials used in this study.

Conclusion

From the present study, it can be concluded that reprocessing dually doped ZnO results in reducing the thermal conductivity from 7 W/m K to 3.5 W/m K. This reduction is due to an increase in porosity and a wider distribution of grain sizes in the reprocessed material leading to scattering a wider spectrum of phonons. The low power factor observed for this material is most likely due to insufficient substitution of Al and Ga for Zn atoms. It is probable that the increased porosity in the reprocessed sample led to increased phonon scatter, which would decrease the power factor. Increasing the calcination temperature and sintering temperature by 200K should increase the likelihood of substitution which will in turn lead to a higher power factor.

Acknowledgments

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