

## Effect of Al Doping Concentration to the Physical and Thermoelectric Properties of Zinc Oxide

<sup>1</sup>J.H Lim, <sup>2</sup>C.K.Yeoh, <sup>3</sup>P.L. Teh, <sup>4</sup>A.Chik and <sup>5</sup>W.M. Arif

<sup>1</sup>School of Materials Engineering, Universiti Malaysia Perlis, 02600 Jejawi, Perlis.

**Abstract:** In this paper, different Al concentrations were used to study the impact Al-doping on the structural and thermoelectric properties of zinc oxide (ZnO). The thermoelectric property was related to the Seebeck coefficient (thermopower) of the materials. Therefore, doped zinc oxide had been studied to determine the effect of doping for an existing materials for thermoelectric properties. In this research, the samples were prepared by solid-state method for zinc oxide (ZnO) with different concentration of Al-doping. The concentration of Al-doping for zinc oxide was within the range 2wt% to 4wt%. Different concentrations of Al-doping were mixed with zinc oxide and shape into pellets through cold hydraulic press machine with diameter 11mm and thickness 5mm. The green compacts were sintered at 800°C and then proceed to characterization. The Al-doped ZnO were tests through X-ray diffraction to determine any phase change with different concentration of Al-doping. Besides, grain size, density and Seebeck coefficient of Al-doped ZnO were examined to study the influence of Al-doping. It was observed that the 4wt% Al-doped ZnO had the lower value of density 4.58g/cm<sup>3</sup>. The microstructure of the Al-doped ZnO show the 2wt% Al-doped had the higher average grain of 4.9µm. Al-doped ZnO had the higher value of Seebeck coefficient of -48.9µV/K and decreased to -48.1µV/K and -47.8µV/K for 3wt% and 4wt% Al-doped ZnO respectively. As the Al-doping concentration increased shown fine morphology but low density and Seebeck coefficient.

**Key words:** Al-doped ZnO, density, morphology, grain size, Seebeck coefficient.

### INTRODUCTION

Recently, thermoelectric materials have gain interest as potential materials in the field of thermoelectric power generation devices. Thermoelectric device could used to convert heat into electrical energy and vice versa (David M.Rowe, 1995). In industrial processes, thermoelectric materials are used to improve the performance and efficiency conversion of heat into electricity. Generally metal based thermo generator is not suitable because it deteriorate at high temperature. Thus, oxide based materials like zinc oxide (ZnO) become potential material in thermoelectric application. However, the performance and efficiency of zinc oxide is quite low (S.J.Pearton *et al*, 2003). The conversion efficiency of thermoelectric material depends on the thermoelectric figure of merit (ZT) of the material properties (C.Godart *et al*, 2009). The thermoelectric figure of merit defined as given in Equation 1, where S is the Seebeck coefficient,  $\sigma$  is the electrical conductivity and  $\lambda$  is the thermal conductivity.

$$ZT = \sigma S^2 / \lambda \quad (1)$$

The Seebeck coefficient also term as thermoelectric power or thermopower effect describes the fact that a temperature gradient drives the diffusion of charged carriers which in turn creates a voltage (T.M.Tritt, 2002). The Seebeck coefficient of a material depends on the material's temperature and crystal structure. Fundamentally, the thermopower is a measure of the amount of net entropy transported per carrier (Ali Ahakouri, 2011). The major contributors to the transfer of entropy in the presence of a temperature gradient originate from diffusion and/or phonon drag effects.

Zinc oxide is group II-VI semiconductor where the II-VI compounds semiconductors had been an interesting classification of semiconductors. The crystal structure for II-VI compounds generally crystallize in cubic or hexagonal structure. These compounds mostly occur in a wide range of band gap and lattice constants. In term of thermal properties, zinc oxide is a good thermal conductor with a high thermal capacity. This property of zinc oxide has leads to become very important in the rubber industry where it is a major component of tires (G.S.Nolas *et al*, 2001). Zinc oxide is a degenerate semiconductor with a direct band gap of 3.22eV at room temperature, large exciton binding energy (60 meV) and optical transparency (S.J.Pearton, 2003). The properties of ZnO with a direct band gap and high exciton binding energy are much higher than those of other widely used wide band gap materials. Zinc oxide had the advantages associated with its large band gap which include high breakdown voltages. Besides, zinc oxide also had the ability to sustain large electric fields, low noise enervation and high-power operation (Berardan, 2010).

Zinc oxide is an attractive material in thermoelectric field. The transition metal oxides show the same order of magnitude as the semiconductors that it can exhibit good thermoelectric properties. The advantage of using these oxides is the greater diversity of compositions and the opportunities for control of carriers by doping (Eun S. Shim *et al*, 2002). Doped zinc oxide considered as one of the most studied oxides today. High-mobility carriers are most desirable in order to have the highest electrical conductivity for a given carrier concentration. It has been proposed for a variety of applications spanning from thermoelectric, sensors, catalysis to transparent electronic materials (S. Adachi, 2005). Since Xiurong *et al* (Xiurong Qu *et al*, 2011) reported that with increasing Al doping concentration, the electrical conductivity increases and the thermal conductivity decreases significantly, where the Seebeck coefficient decreases slightly.

In order to produce an efficient thermoelectric energy conversion, the following three physical properties are required for thermoelectric materials: (1) low thermal conductivity, which is necessary to introduce a large temperature difference into both ends of the material, (2) high electrical conductivity, which is required to reduce the internal resistance of the material, and (3) large thermoelectromotive force (Seebeck coefficient,  $S$ ), which is needed to obtain a high voltage (David M. Rowe, 1995). Doping is the influence factor to improve the thermoelectric performance of the existing materials. It is well known that the addition of doping is a feasible route to optimizing the thermoelectric performance. In the present work, the effects of Al doping on the Seebeck coefficient and physical properties of ZnO are investigated.

## MATERIALS AND METHODOLOGY

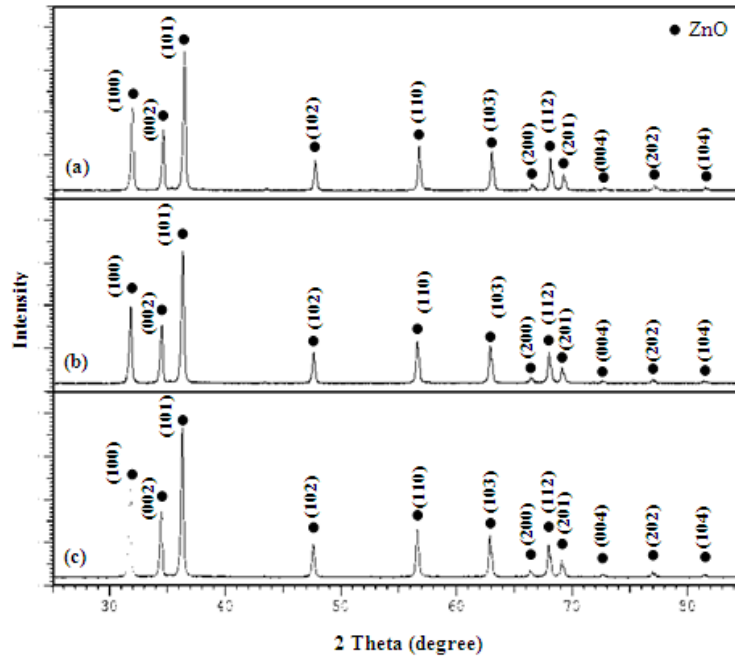
The sample composition of 2wt%, 3wt% and 4wt% Al-doped ZnO were prepared by solid state method. Zinc oxide (ZnO) powder and alumina ( $Al_2O_3$ ) powder as the doping materials were used as the starting materials. The samples were compacted into pellets of 5mm of thickness and 15mm in diameter. All samples were pressed by using a cold hydraulic press machine at 100MPa for 5min. Then, the green compact were sintered at 800°C for 4 hours with heating and cooling rate of 10°C/min.

The synthesized samples of Al-doped ZnO were characterized by X-ray diffraction analysis (Shinadzu XRD 2000). The exposed surface was sequentially polished with SiC abrasive paper and diamond pastes (1 $\mu$ m). The polished specimens were thermally etched at 700°C for 1 hour to develop the microstructures. Then, the morphology of the etched samples was observed by a scanning electron microscope (SEM JEOL JSM-6460 LA Jeol Japan). The average grain size was estimated from the linear intercept length that was determined from the microstructure (H.E. Exner and H.L. Lukas, 1971). The density of the bulk specimens were also measured using the Archimedes immersion technique. The Seebeck coefficient was determined by measures the voltage induced in response to a temperature difference.

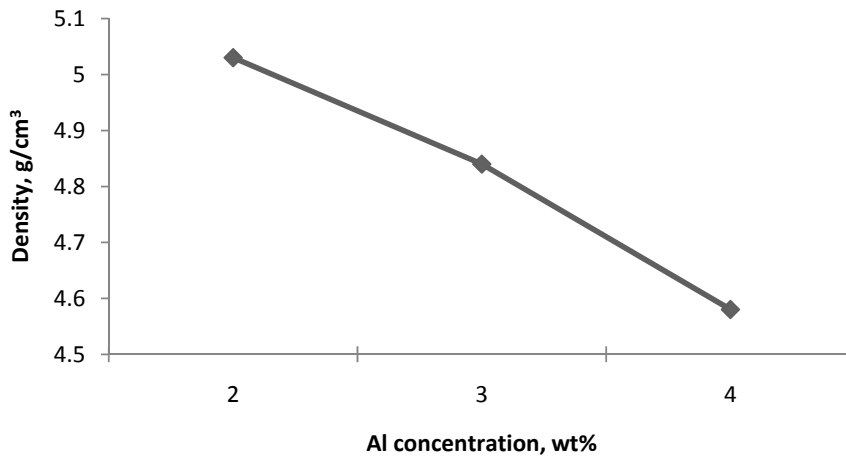
## RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction patterns of Al-doped ZnO with different concentration of Al. All the samples exhibit a polycrystalline hexagonal structure. The peaks are identified as the plane reflections for wurtzite phase of zinc oxide according to the standard JCPDS data file (No. 36-1451), impurity peaks were not detected. This is similar to test results reported by Lihua Zhang *et al* (Lihua Zhang *et al*, 2008) where impurity peaks were not detected. They found all the peaks of the Al-doped ZnO correspond to the standard JCPDS data file (No. 36-1451). The dopants did not form significant amounts of additional crystalline phases since no additional peaks were found.

The density of the Al-doped ZnO after sintered for 4 hours are shown in Figure 2 as a function of Al concentration. It can be seen that with the increasing Al concentration from 2wt% to 4wt%, the density decreases significantly. The 2wt% Al-doped ZnO had the higher value of density of 5.05g/cm<sup>3</sup>. The density of Al-doped ZnO decreases to 4.89g/cm<sup>3</sup> and 4.58g/cm<sup>3</sup> when the Al-doping concentration increases to 3wt% and 4wt% respectively. Byungjin Hwang *et al* (Byungjin Hwang *et al*, 2011) have studied the densification of Al-doped ZnO with the Al-doping concentration 1wt% to 5wt%. The decrease in density may possibly due to the low density of alumina 3.19g/cm<sup>3</sup> that cause the loss in mass of the Al doped ZnO. They found the density of Al doped ZnO decrease as the Al-doping concentration increases. The density of 2wt% Al-doped ZnO was 5.1g/cm<sup>3</sup> and decreases to 4.9g/cm<sup>3</sup>, 4.6g/cm<sup>3</sup> at 3wt% Al doped ZnO and 4wt% Al-doped ZnO respectively. This is similar to the test results of the experiment.

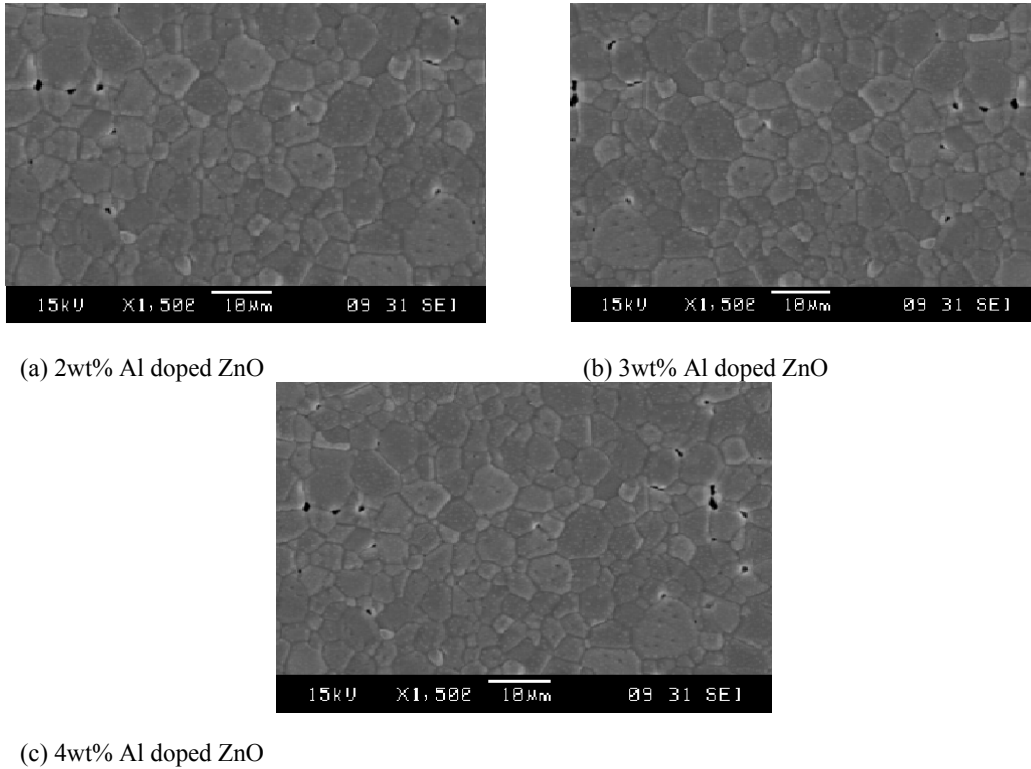


**Fig. 1:** X-ray diffraction pattern of Al-doped ZnO with different Al doping concentration (a) 2wt% (b) 3wt% (c) 4wt%.

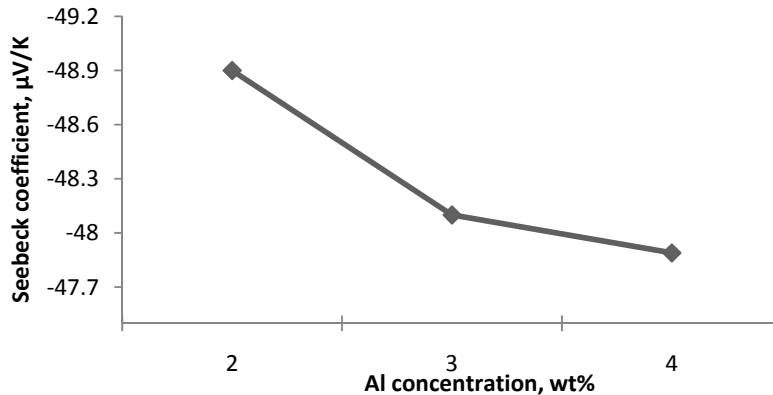


**Fig. 2:** Densities of Al doped ZnO as a function of the Al-doping concentration.

Morphology of Al doped ZnO with different Al-doping concentrations are given in Figure 3. The microstructural indicated that increasing concentration of Al-doping, even with very low amounts added to the starting composition, strongly influenced the grain size ( $D$ ). The grain size of Al-doped ZnO decreases with the increases of Al-doping amounts is clearly evident. The average grain size of 2wt% Al doped ZnO was 4.9 $\mu$ m. The average grain size decreases to 4.7 $\mu$ m and 4.2 $\mu$ m for 3wt% Al doped ZnO and 4wt% Al doped ZnO respectively. This was similar to the test results of S.Bernik *et al* (S. Bernik and N. Daneu, 2007) reported. They found that the average grain size for 2wt% Al doped ZnO was 5.9 $\mu$ m and decreases to 3.7 $\mu$ m when the Al-doping concentration increases to 8wt% above.



**Fig. 3:** Morphology of Al doped ZnO with different Al-doping concentrations.



**Fig. 4:** Seebeck coefficient of Al doped ZnO with different Al-doping concentrations.

The Seebeck coefficient of the Al-doped ZnO after sintered for 4 hours are shown in Figure 4 as a function of Al concentration. The negative sign of the Seebeck coefficient show the sample as the n-type semiconductor. It can be seen that with the increasing Al concentration from 2wt% to 4wt%, the Seebeck coefficient decreases slightly. Based on Figure 4, it indicated that the 2wt% Al-doped ZnO had the higher value of Seebeck coefficient of  $-48.9\mu\text{V/K}$ . The Seebeck coefficient decreased to  $-48.1\mu\text{V/K}$  and  $-47.8\mu\text{V/K}$  for 3wt% and 4wt% Al-doped ZnO respectively. The Seebeck coefficient of Al-doped ZnO decrease with increasing concentration of Al-doping may due to the increase of Al-doping had cause the materials change to metal. This was similar to test results reported by Xiurong Qu *et al* (Xiurong Qu *et al*, 2011) that the Seebeck coefficient decreases with increasing the concentration of Al-doping. The Seebeck coefficient reported by them was higher and it may because they using chemical co-deposition method. They found the Seebeck coefficient  $-180\mu\text{V/K}$  for 1wt% Al-doped ZnO and slightly reduced to  $-175\mu\text{V/K}$  for 3wt% Al-doped ZnO.

### Conclusion:

The effect of Al-doping concentration to the phase formation, density, microstructure and Seebeck coefficient of ZnO were investigated experimentally. The increase of concentration of Al-doping has a significant effect to the density, microstructure and Seebeck coefficient of ZnO. The density, microstructure and Seebeck coefficient of ZnO decreased and reached lower value when the Al-doping concentration increases to 4wt%.

### ACKNOWLEDGEMENT

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