

# Thermoelectric properties, phase analysis, microstructural investigation and lattice parameters c/a ratio of Al<sup>3+</sup> and In<sup>3+</sup> dual-doped zinc oxide-based ceramics sintered at high temperature under an argon atmosphere

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## ABSTRACT

Composition in (Zn<sub>0.98-y</sub>In<sub>y</sub>) (y = 0.05, 0.02, 0.01, 0.005) were fabricated via conventional solid-state sintering route under an argon atmosphere at 1400 °C for 10 h (h) their phases, microstructures and thermoelectrical properties were investigated. Single phase ceramics were formed for the composition with y ≤ 0.05. The highest power factor (PF) of 481.8 μW K<sup>-2</sup> m<sup>-1</sup> ± 0.2, Seebeck coefficient −98.08 μV K<sup>-1</sup> ± 0.2 and electrical resistivity (ρ) of 1.997 mΩ cm ± 0.2 was obtained for x = 0.02, y = 0.005 i.e., (Zn<sub>0.975</sub>Al<sub>0.02</sub>In<sub>0.005</sub>)O. It is studied that PF is a function of lattice parameter c/a ratio. The resistivities of all the compositions were tuned. These tuned resistivities will be helpful for future thermoelectric devices.

## 1. Introduction

ZnO is known as one of the most important *n*-type thermoelectric material and has unique physical and chemical properties such as high Seebeck coefficient (SC) as well high carrier mobility [1]. Thermoelectric materials are able to convert waste heat directly into useful energy without disturbing environment. Zinc Oxide (ZnO) is one of the best thermoelectric material which works in high-temperature range. Due to its unique chemical and physical properties, high temperature stability, high SC, non-toxic and high photostability, it is called multifunctional material [2]. Also, the low cost of ZnO and easy availability are promising for thermoelectric applications [3]. The transport properties of ZnO are tunable via different suitable doping [4,5]. ZnO has wurtzite structure and hence the thermal conductivity of ZnO is high, which is the main disadvantage of this material [6]. There are number of elements which can be doped with ZnO either single doped such as Al [7], Bi [8], Co [9], In [10] or even dual doping is also possible [7,8]. ZnO dually doped has the highest Seebeck coefficient i.e., −380 μV K<sup>-1</sup> to −400 μV K<sup>-1</sup> [9,10]. For improving the electrical conductivity of

ZnO, elements of group 3 such as Aluminum (Al), Gallium (Ga), Boron (B) and Indium (In) are usually doped with ZnO [11]. ZnO is also widely used in LASER, optoelectronics technology [12], gas sensors and power generators [13,14].

So far, different research groups used different techniques and different concentrations to obtain a highest power factor as well SC. Jung et al., achieved a PF of 9.18 × 10<sup>-4</sup> W m<sup>-1</sup> K<sup>-2</sup> at 1050 K for Ga doped ZnO [15]. Mele et al., achieved a SC of −65 μV/K and PF of 0.13 × 10<sup>-3</sup> W m<sup>-1</sup> K<sup>-2</sup> at 300 K [16]. Jood et al., obtained a SC of −310 μV/K and PF of 12 × 10<sup>-3</sup> μW m<sup>-1</sup> K<sup>-2</sup> at 1000 K [17]. Pradyumn et al., obtained a PF ~ 0.57 × 10<sup>-4</sup> W m<sup>-1</sup> K<sup>-2</sup> at 973 K [18]. Yang et al., in 2017 obtained a PF ~ 5.3 × 10<sup>-4</sup> W m<sup>-1</sup> K<sup>-2</sup> at 750 K [19] for Al-doped ZnO by field assisted deforming. D. Berardern in 2010 attempted to get a high PF via using different techniques. He studied different thermoelectric properties of Al-doped ZnO in air as well N<sub>2</sub> atmosphere [20]. Berardern studied that there is a large difference in thermoelectric properties between air and N<sub>2</sub> prepared samples. The N<sub>2</sub> prepared samples electrical resistivity was between of 1–2 mΩ cm. Mati et al., [21] studied PF of Al, Ga doped ZnO sintered

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both in air and argon atmosphere and it was found that the *PF* of air sintered samples was 1.4 times higher than argon atmosphere for the same composition.  $\text{Ga}_2\text{O}_3$  is a transparent conducting oxide and have a band gap of 4.8 eV. The band gap of  $\text{In}_2\text{O}_3$  is 3.75 eV. The direct band gap of  $\text{In}_2\text{O}_3$  is near to the direct band gap of ZnO and therefore we doped  $\text{Al}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  with ZnO and sintered in an argon atmosphere in this article.

In the present study, we have focused to achieve a high *SC* as well as higher *PF* ( $S^2\sigma$ ) without disturbing electrical and thermal properties of the co-doped ZnO sintered in an argon atmosphere. We observed that *PF* is a function of *c/a* lattice ratio. Using argon gas as sintering media the resistivities of all compositions were lowered. The tuned and lower electrical resistivities,  $\rho$ , will be beneficial for future thermoelectric devices.

## 2. Experimental procedure

### 2.1. Preparation of compositions

Solid-state reaction were used to synthesized samples of  $(\text{Zn}_{0.98-y}\text{Al}_{0.02}\text{In}_y)\text{O}$  ceramics, with  $y = 0.05, 0.02, 0.01, 0.005$ . The starting materials were ZnO (99.5%),  $\text{In}_2\text{O}_3$  (98%) and  $\text{Al}_2\text{O}_3$  (99.5%) buy with the same provider Sinopharm Group, Co., Ltd. The raw materials were mixed in stoichiometric ratios and ball milled for 17 h using absolute ethanol as lubricant and zirconia ball as grinding media. The cup in which the raw materials were mixed is made of liquid silicone rubber. The speed of ball mill machine was kept 205 rpm. After 17 h of ball milling the slurries were put into four different labeled trays and these trays were put in a DGX-92438 furnace kept at  $\sim 105^\circ\text{C}$  overnight. The dried powders were sieved via mesh # 140. The sieved powders were press into small pellets at 10 MPa via mechanical press. The small pellets were sintered in an argon gas as a sintering media at  $1400^\circ\text{C}$  for 10 h. The small pellets were cut into rectangular columns bars of  $12.0\text{ mm} \times 2.0\text{ mm} \times 2.0\text{ mm}$  for measuring different thermoelectric properties. The remaining pieces of the small pellets were crushed into small pieces and powders for measuring surface topography via scanning electron microscopy (SEM, Hitachi S-4800) and phase analysis.

### 2.2. Characterization of compositions

The overall surface structures were studied by powder x-ray diffraction (XRD) via Brucker AXS D8 ADVANCE diffractometer (Toshiba, Japan) using  $\text{Cu-K}\alpha$  radiation with 40 kV and 100 mA (Wavelength  $\lambda = 1.5418\text{ \AA}$ ) (at a step  $0.02^\circ$  per minute) over an angular range  $2\theta = 20\text{--}80^\circ$ . The measurements were performed at room temperature. The surface topography was studied by SEM. The % weighed of all compositions was confirmed via EDAX mounted SEM.

### 2.3. Measurements of thermoelectric properties

The argon gas sintered compositions were cut into rectangular columns bars  $12.0\text{ mm} \times 2.0\text{ mm} \times 2.0\text{ mm}$  for measuring different thermoelectric properties. The *SC* was calculated from Relative Seebeck coefficient. The  $\rho$  were measured using four-point probe method via LSR-3. The *SC* was measured by the temperature difference between the upper and lower heaters of the LSR-3. The *PF* were measured by *SC* and electrical conductivities ( $\sigma$ ) as,

$$P, F = S^2\sigma \quad (1)$$

where  $\sigma$  represents electrical conductivity and *S* is the absolute Seebeck coefficient. The  $\rho$  and *SC* were measured under helium conditions via LSR-3. Different thermoelectric properties were measured in temperature range  $100\text{--}700^\circ\text{C}$ .

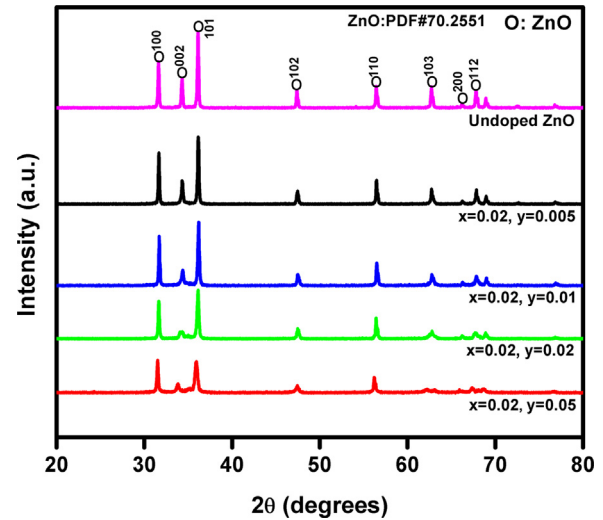


Fig. 1. Powder X-ray diffraction (XRD) for the nominal formula  $(\text{Zn}_{1-x-y}\text{Al}_x\text{In}_y)\text{O}$ , with  $x = 0.02$ ,  $y = 0.05, 0.02, 0.01, 0.005$  and undoped ZnO.

## 3. Results and discussions

The powder X-ray diffraction (XRD) for different doped and pure ZnO has been shown in Fig. 1. The measuring angle used  $2\theta = 20\text{--}80^\circ$ , while the scanning rate was  $2$  at a step of  $0.02^\circ$  per minute. The main peaks for all composition matches with PDF# 70.2551 for ZnO. The  $(\text{Zn}_{0.98-y}\text{Al}_{0.02}\text{In}_y)\text{O}$  ceramics, the composition with  $x = 0.02$ ,  $y = 0.05$  has the lowest peak intensity. The reason for the lower peak intensity is the high dopant amount of  $\text{In}^{3+}$  i.e.,  $y = 0.05$ . In single  $\text{Al}_2\text{O}_3$  doped ZnO, there are secondary phases but the intensity of all compositions are high [22]. As Indium (In) concentration decreases the peaks become sharper. For undoped ZnO, the observed peaks are consistent with hexagonal wurtzite structure. Fig. 1 (XRD) shows the composition is basically in sole phase form. Only sharp (high intensity) peaks were obtained for compositions with  $x = 0.02$ ,  $y = 0.02, 0.01, 0.005$  as well for undoped ZnO. The high intensities of XRD peaks pattern showing the better crystallinity of ZnO, leaning at (101) [23, 24]. No secondary or unknown phases were studied. The absence of secondary and unknown phases means that  $\text{Al}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  compositions are completely dissolved in ZnO. The effect of making secondary phases has been demolished by  $\text{In}_2\text{O}_3$ .

The unavailability of  $\text{ZnAl}_2\text{O}_4$  indicates that there is no reaction take place between ZnO and  $\text{Al}_2\text{O}_3$ . We studied that with decreasing amount of  $\text{In}_2\text{O}_3$  the peaks are becoming sharper. The maximum intensity has been observed for undoped ZnO in (101) direction. As discussed above that by decreasing the  $\text{In}_2\text{O}_3$  concentrations, the intensity of the peaks increases. The changes in the XRD peaks are thus caused by  $\text{In}_2\text{O}_3$  (Table 1).

Table 2 shows the *c/a* ratio for all compositions for nominal formula  $(\text{Zn}_{0.98-y}\text{Al}_{0.02}\text{In}_y)\text{O}$ , with  $x = 0.02$ ,  $y = 0.00, 0.05, 0.02, 0.01, 0.005$ . The highest value for *c/a* ratio was studied for composition with  $x = 0.02$  and  $y = 0.05$ . From Table 2 it is evident that for the higher concentration of Indium (In), the *c/a* ratio has the maximum value. The

Table 1  
Lattice parameters and volumes of  $(\text{Zn}_{0.98-y}\text{Al}_{0.02}\text{In}_y)\text{O}$ , where  $y = 0.00, 0.05, 0.02, 0.01, 0.005$ .

x	y	a = b (Å)	c (Å)	v (Å) <sup>3</sup>
0.00	0.00	3.26809	5.24779	48.54
0.02	0.05	3.25713	5.21560	48.32
0.02	0.02	3.25505	5.20346	47.75
0.02	0.01	3.25459	5.21057	47.80
0.02	0.005	3.25713	5.20935	47.75

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