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Modify thermoelectric properties of ZnO with ZrO_2 nanoparticles additive

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Abstract:

Solid-state reaction processing technique was used to prepare ZnO-doped ZrO2 samples. The XRD patterns of the samples showed that Zr^{4+} ions substituted Zn^{2+} ions in the Zinc oxide structure. The SEM results revealed that the grain size of the Zinc oxide decreases with increasing ZrO_2 content. Thermoelectric measurements show that the addition of ZrO_2 to ZnO led to a significant increase in the electrical conductivity and a decrease in the absolute value of the Seebeck coefficient. Significant reduction of the thermal conductivity was observed as compared to pure ZnO sample. The figure of merit *ZT* values of Zno-doped ZrO_2 samples are higher than the ZnO pure sample, specially at high temperatures , this demonstrated that the ZrO_2 addition is fairly effective for enhancing thermoelectric properties.

Keywords:

Thermoelectric; Zinc oxide; Thermal conductivity; Electrical conductivity; Seebeck coefficient; Figure of merit.

Introduction:

Thermoelectric materials that have a sufficiently strong thermoelectric effect could be used for applications including power generation, refrigeration and a variety of other applications in electronic industry. Thermoelectric (TE) materials can directly convert temperature difference into electric power due to the Seebeck effect [1]. In **1823** Seebeck

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reported the results of experiments in which a compass needle was deflected if placed in the vicinity of a closed loop, formed from two dissimilar conductors, when one of the junctions was heated. The Seebeck coefficient is expressed in volts per degree, or more often in micro volts per degree μVK^{-1} [2].

In the 1950s, Abraham Ioffe showed that doped semiconductors showed a much larger thermoelectric effect than other materials. This led to research of binary semiconductors as thermoelectric materials in the 1950s, with Bi2Te3 having the greatest thermoelectric effect at
room temperature. The research led a good understanding of the properties displayed by a good
thermoelectric material. It was not until the 1990s that interest increased again due to new materials discoveries with the potential for excellent thermoelectric properties [3,4].

The energy conversion efficiency of a material is characterized by the thermoelectric figure of merit that obtained from Eq. 1.

$$ZT = \alpha^2 \sigma T/k \qquad (1)$$

Where σ, α, k, and T are the electrical conductivity, seebeck coefficient, thermal conductivity and absolute temperature, respectively [5].
Approaches to improve thermoelectric conversion efficiency are driven by the need to maximize the Seebeck coefficient, α, and to balance the competing requirements of low electrical resistivity, 1/σ, and low thermal conductivity, k [6].
Recent advances have shown that *ZT* can be enhanced in nanoscale systems by taking advantage of phonon scattering at interfaces to reduce thermal conductivity and quantum confinement and carrier scattering effects to enhance the power factor,$\alpha^2\sigma$ [6]. Various processing methods, such as mechanical alloying, sol–gel and polymerized complex synthesis methods have been used to produce nanostructured oxide TE materials. Currently, reasonably high ZT is only found in p-type oxide TE materials. The progress in developing n-type oxide TE materials with comparable ZT is still lacking, which calls for more research effort in this area [7,8].
Metal oxides should be advantageous for high-temperature TE applications because of their high thermal stability and excellent oxidation resistance .ZnO is the one of the most important thermoelectric materials and has an extensive application due to its unique properties such as high carrier mobility and Seebeck coefficient [9-11].
In previous studies Al_2O_3 doped to Zinc oxide and their thermoelectric properties were investigated, but in this work we studied the effect of ZrO_2 nanoparticles on the thermoelectric properties of ZnO.

Data and Materials and research methodology:

The sample with a composition of ZnO + x wt % ZrO (x= 0.5, 1, 1.5, 2) were prepared by solid state reaction method. The high purity raw materials, ZrO_2 (>99% purity, Merck, Germany) and ZnO (>99% purity, Merck, Germany) powders, were weighed in stoichiometric composition. Then milling was carried out in a ball mill equipped with a zirconia balls in ethanol at room temperature under atmosphere with a rotation speed of 300 rpm. The ball to powder ratio of 20:1 was employed. Afterwards, ethanol and ZrO2

balls were removed and the slurry was dried under vacuum at 80 ◦C for 5 h. The resulting mixture was calcined at 850°C for 10 h. The mixture was milled again at attrition mill and the required amount of ZrO_2 balls and Polyvinyl alcohol (PVA, Sigma-Aldrich) were mixed with the calcined powder for 2 h in ethanol then dried at 80°C in an oven for 5 h. The dried powders were pressed into pellets (cylinder) with diameter of 10mm and thickness of 15mm using a double press at a force 2KN. The specimens were sintered at 1400°C for 5 h, and then cooled in the furnace to room temperature.

X-ray diffraction (XRD Brucker D8-Advance with CuKa tube) method using Cu Kα radiation (wavelength λ=1.5418 A˚) was done on the samples for the structural determination. The microstructure of the as-sintered samples was investigated using a scanning electron microscope (SEM).

Electrical conductivity of the samples was measured over the temperature range of 300k – 873k by multimeter. In order to plot the different electrical potential as a function of temperature of the samples; the temperature of the one side of the samples were fixed at 50 °C but in the other side the temperature were gradually increased up to 600 °C by step of 50 °C, while the different electrical potential in each step was measured. Finally the seaback coefficient obtained via measuring the slops of the plot at each temperature.

Results and Analysis:

Fig. 1 shows the X-ray diffraction patterns of ZnO + x wt % ZrO (x= 0.5, 1, 1.5, 2) samples. All samples contain ZnO as the main phase and Zn_2ZrO_4 as a minority secondary phase. However when Zr additive concentrations were just 1.5 wt % , then the Zn_2ZrO_4 diffraction peaks were visible. It can be seen that the XRD diffraction patterns of the doped samples have been changed. In fact the intensity of the peaks altered and the diffraction angle shifted to lower angle due to higher lattice constant of Zr^{4+} rather than Zn^{2+}.

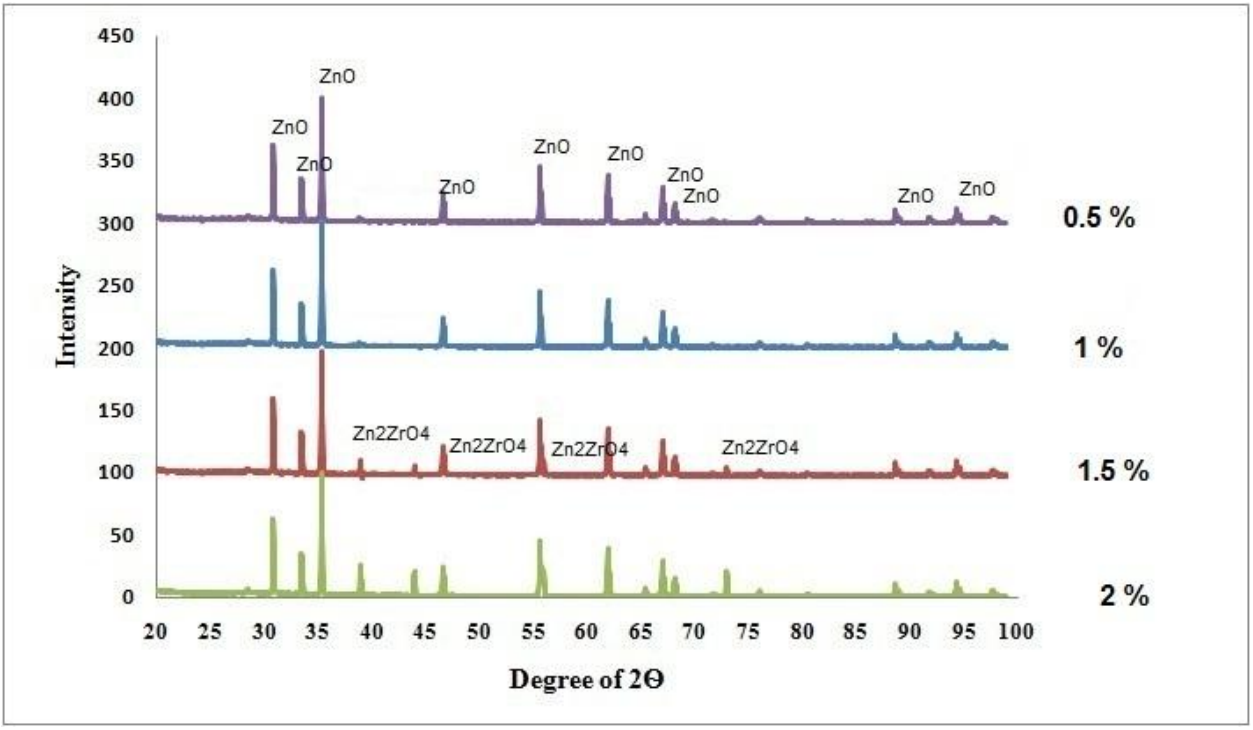

Fig. 1 XRD pattern of the samples with different amount of ZrO_2 added.

The SEM images in Fig. 2 (A-D) show the microstructure of the sintered samples. It is clearly apparent that the ZnO grain size increases with the small addition of ZrO_2 because the substitution of Zr^{4+} for Zn^{2+} increases the activity of ZnO by means of distortion of the ZnO lattice, which is beneficial to grain growth in doped samples. In contrast, the ZnO grain size for high ZrO_2 content (> 1 wt %) gradually decreases by further increasing the ZrO_2 content. This is attributed to the pinning effect caused by the Zn_2ZrO_4 particles on grain boundaries as well as to the dragging effect between the added ZrO_2 and grain boundaries, resulting in a reduction in the mobility of ZnO grain boundaries.

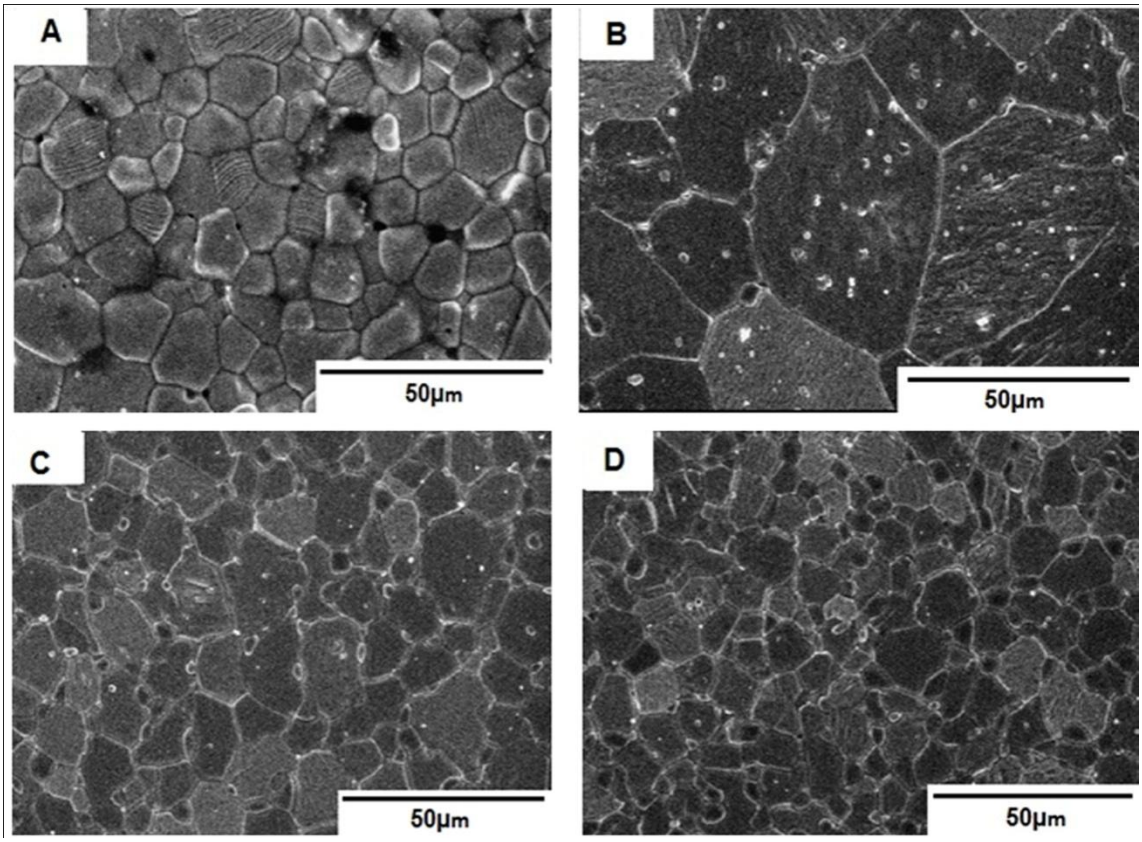

Fig. 2 SEM images from the surface (a)0 %, (b) 0.5 %, (c) 1 %, and (d) 1.5 % Zr added samples.

Fig. 3 shows the electrical conductivity as a function of temperature of the samples. The electrical conductivity of the doped samples slightly increased with increasing temperature, indicating semiconducting behavior [12]. Also the electrical conductivity in ZrO_2 doped samples is higher than of pure sample. This can be explained by considering various competing factors affecting the electrical conductivity as follows. (1) The addition

of Zn^{4+} for Zn^{2+} may increase the electron concentration of the system to compensate for the electric charge balance, thereby increasing the electrical conductivity. (2) ZrO_2 addition leads to a decrease in the grain size, and to an increase in Zn_2ZrO_4. This is responsible for the decrease in the time between the scattering events of charge carriers, thus decreasing the electrical conductivity [13,14]. It can be said that the first case occurs more than the latter, therefore electrical conductivity increases.

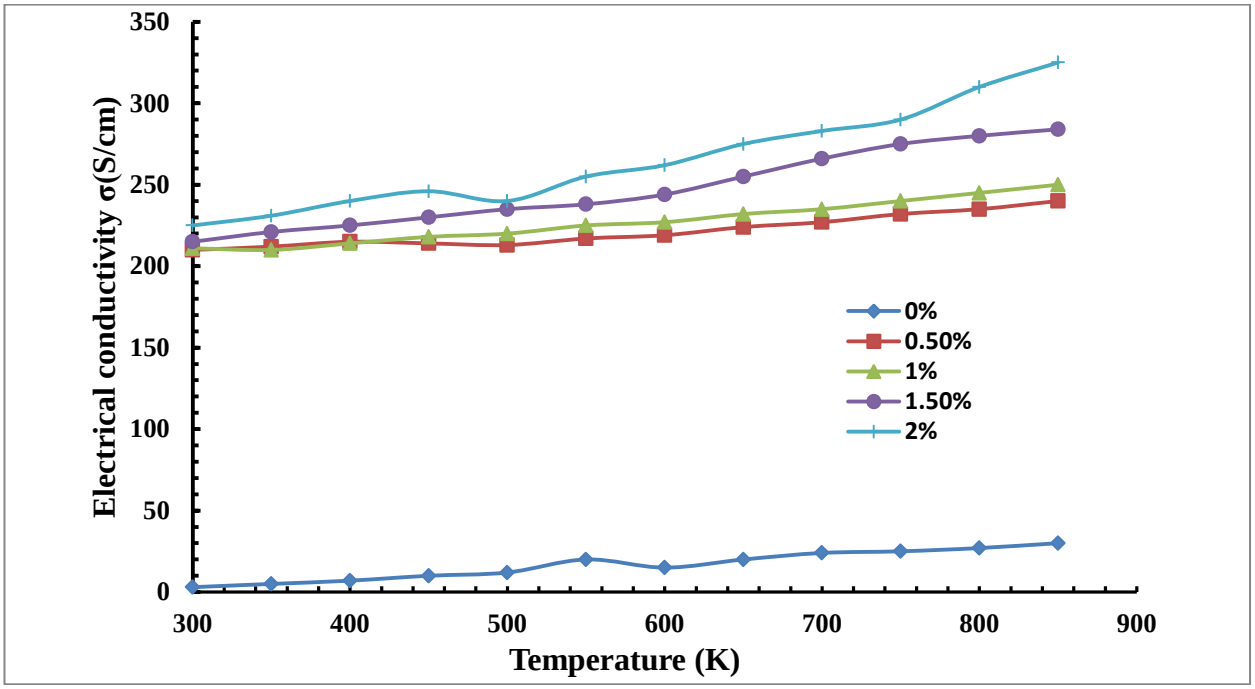

Fig. 3 Electrical conductivity as a function of temperature for the $Zn_{1-x}Zr_xO$ samples.

Fig. 4 shows the temperature dependence of the Seebeck coefficient for the samples. The sign of the Seebeck coefficient is negative over the whole temperature range for all the samples, indicating that the major conductivity carriers are electrons. The absolute value of Seebeck coefficient of all the samples increased with temperature and decreased rapidly with the increase of ZrO_2 content added. This can be explained by broadband model, the value of the Seebeck coefficient in common semiconductors decreases with increasing carrier density. Based on a simplified broadband model, the Seebeck coefficient (α) of the extrinsic n-type semiconductors with negligible hole conduction devices can be expressed as Eq. 2 [15].

$$S = -\frac{k}{e}\left[\ln\frac{N_c}{n} + A\right] \qquad (2)$$

Where *k* is the Boltzmann constant, *n* the electron concentration, *e* the electric charge of the carrier, *N*v the density of state, and *A* is a transport constant, typically $0 \leq A \leq 2$.

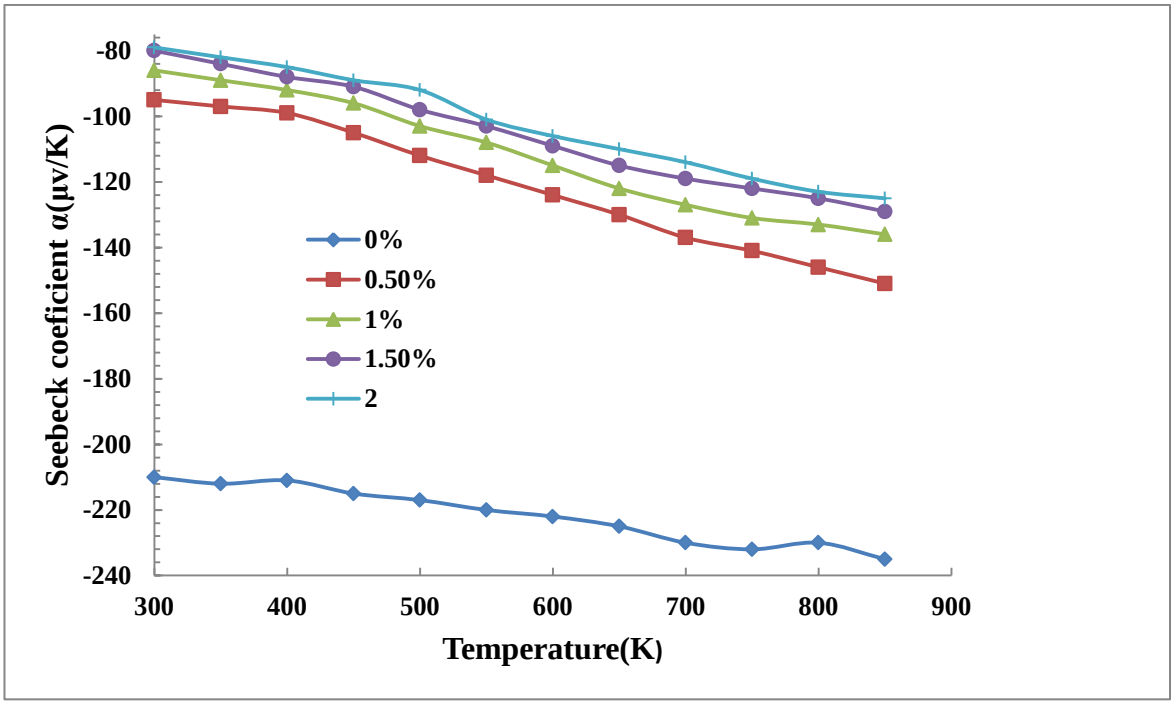

Fig.4 seebeck coefficient as a function of temperature for the $Zn_{1-x}Zr_xO$ samples.

The variation of thermal conductivity k with temperature for the various samples is shown in fig. 5. It is clearly apparent that Increase the temperature reduces the thermal conductivity in all samples. It is due to the fact that thermal conductivity is dominated by phonon transfer [16]. It is also noted that the thermal conductivity values of Zr-doped samples are lower than the undoped sample only at low temperature. This agrees with the theoretical prediction that at low temperature, grain boundary and impurity scattering dominate phonon transfer and determine the final thermal conductivity [17].

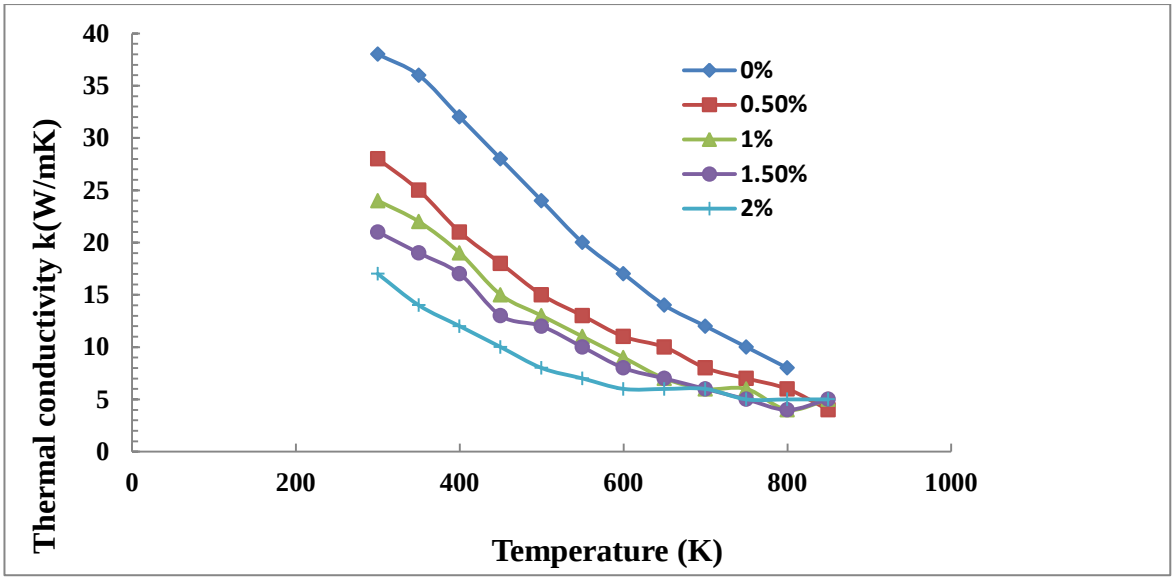

Fig. 5 temperature dependence of the thermal conductivity of the $Zn_{1-x}Zr_xO$ samples.

In fig. 6, the figure of merit ZT for all the samples at desired temperatures calculated and plotted using the obtained data and an equation $ZT = \alpha^2\sigma T/k$. According to this figure it can be concluded that the thermoelectric properties of ZnO were improved by adding ZrO_2 additive. In addition this improvement was remarkable at higher temperature (T > 823°K) while having no such effect in lower temperatures. It also is clear that performance thermoelectric of Zinc oxide increased with increasing temperature, thus ZnO doped ZrO_2 can be used in high temperature applications.

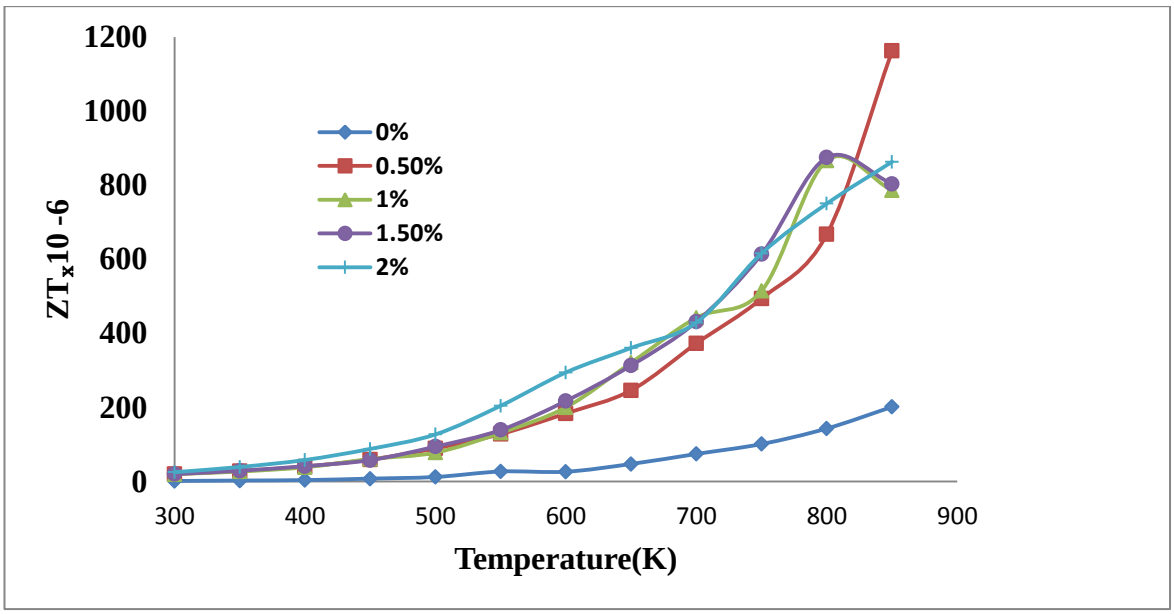

Fig. 6 Temperature dependence of the ZT of $Zn_{1-x}Zr_xO$ samples.

Conclusion:

The absolute value of the Seebeck coefficient decreased and electrical conductivity increased with increasing ZrO_2 content mainly because an increase in electron concentration and the thermal conductivity decreased with the increase of the amount of ZrO_2 added due to enhanced phonon scattering.

The addition of Zirconium nanoparticles for Zinc in solid solution $Zn_{1-x}Zr_xO$ improved thermoelectric performance of Zinc oxide. In fact, the figure of merit of the ZrO_2 added samples was significantly improved compared with the pure ZnO sample. The thermoelectric figure of merit was maximized to value of 1162.0 at 873K for the 1 wt % Zr added sample.

According to the results for the thermal conductivity can be conclude, zirconium atom is suitable for doping to reduce the thermal conductivity since its atomic weight and ionic reduce are very high. In this way that penetrates to the lattice of Zinc oxide and distortion its crystal structure, therefore reduces the phonon scattering greatly and decrease the thermal conductivity. However, the use of heavier oxides may give better results.

Acknowledgment:

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