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Research paper

A review of thermoelectric ZnO nanostructured ceramics for energy recovery

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Abstract

The thermoelectric devices have the ability to convert heat energy into electrical energy without required moving components, having good reliability however their performance depends on material selections. The advances in the development of thermoelectric materials have highlighted to increase the technology's energy efficiency and waste heat recovery potential at elevated temperatures. The fabrication of these thermoelectric materials depends on the type of these materials and the properties using to evaluate these kind of materials such as thermopower (Seebeck effect), electrical and thermal conductivities. Ceramic thermoelectric materials have attracted increased attention as an alternative approach to traditional thermoelectric materials. From these important thermoelectric ceramic materials that can be a candidate for n-type is ZnO doping, which have excellent thermal and chemical stability, as they are promising for high temperature power generator. This review is an effort to study the thermoelectric properties and elements doping related with zinc oxide nanoceramic materials. Effective ZnO dopants and doping strategies to achieve high electrical and thermal conductivities and high carrier concentration are highlighted in this review to enable the advanced zinc oxide applications in thermoelectric power generation.

Keywords*: Thermoelectric; Zinc oxide; Electrical conductivity; Seebeck coefficient; Thermal conductivity.*

1. Introduction

Thermoelectric system is an environment friendly energy conversion technology with advantages of small system size, no pollutants, high reliability and permissibility in a wide range of temperatures. Thermoelectric materials have the ability to directly convert the heat into electricity for power generation applications[8]. The conversion efficiency of these thermoelectric materials was usually determined by the dimensionless figure of merit, $ZT = \sigma S^2 T/K$, where σ, S, T, and K are the electrical conductivity; Seebeck coefficient, absolute temperature; and total thermal conductivity respectively. The term of $S^2\sigma$ is known as power factor [9-11]. The main challenge to improve the thermoelectric performance and separation of S, σ, and κ, which are strongly interrelated[12]

The thermoelectric (TE) module consists of n- and p-type semiconducting materials connected thermally in parallel and electrically in series. The electric potential (Voltage) of these materials generated by a temperature difference is called the Seebeck effect and the proportionality constant is known as Seebeck coefficient. Each thermoelectric materials contains two types of freely moving charges, more electrons (negative charges) and more holes (positive charges). Electrons are the more abundant carrier in n-type materials, holes being the less abundant carrier. In p-type materials, however, holes are the majority carrier, and electrons the minority carrier. If the free charges are positive (p-type), the positive charge will accumulate on the cold which will have a positive potential. In the same way, the negative free charges (n-type) will produce a negative potential at the cold end.

In spite of recent developments in thermoelectric materials research, the potential impact of thermoelectric materials technology for power generations is handicapped by the heavy usage of toxic, expensive, and rare elements such as Te and Se and their low power output[13, 14]. For examples, there are only a few major thermoelectric material systems commercially available now in the world to change the temperature from low to high temperature limited generation including SiGe[15], Bi_2Te_3[16, 17]and PbTe[18]. The applications of these TE materials especially Te-based materials are largely limited by the element resources, toxicity, and material degeneration at high temperatures. Thermoelectric ceramic materials, on the other hand, are promising candidates to circumvent these challenges due to their earth abundance, non-toxicity, cheaper, and high stability of thermal properties. In this review focuses on the thermoelectric properties, the electrical conductivity, seebeck coefficient, thermal conductivity and figure of merit of one important representative oxide, n-type ZnO, which exhibit the best ZT among oxide thermoelectric materials reported to date.

2. N-type nanostructured Zinc oxide dopant

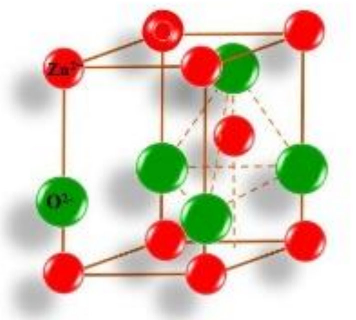

Fig. 1: A wurtzite crystal structure of ZnO.

Zinc Oxide (ZnO) is one of the most important thermoelectric material for energy conversion applications at high temperature. Zinc oxide is an n-type semiconductor having a wide band gap semiconductor between 3.2-3.5 eV with high electron mobility and thermal conductivity. It crystallizes in wurtzite lattice structure at normal conditions. According to this coordination structure, the orbitals of valence electrons of Zn in this kind of oxide can be regarded as sp3 hybrid similar to that of carbon in organic compounds, suggesting a large covalence in the chemical bonding of this kind of component. The lattice constants of zinc oxide crystal are 5.2098Å and 3.2539Å along c-axis and a-axis respectively. In this oxide, O^{2-} and Zn^{2+} ions form hexagonal close packed type sub lattice (Fig. 1). This strange coordination structure as oxide also restricts the elements and their solubility limits for substitution at the Zn positions in ZnO.

Zinc oxide is very stable in wide temperature ranges, cost-effective, non-toxic, and have relatively low environmental impact. Non-doped bulk ZnO is an n-type semiconductor showing increasing electrical conductivity with increasing temperature. However, a small amount of doping with element like Al for example increases electrical conductivity more than three orders of magnitude at room temperature, and changes the conduction behavior from semiconducting to metallic. The major factor limiting of the practical usage of ZnO as a thermoelectric materials is its high value of thermal conductivity *K*. Therefore, some of the strategies proposed in order to lower the *K* value is by increasing phonon scattering along grain boundaries or reducing the oxide particle size.

In technological and engineering perspectives, nanostructuring has been proven to provide an effective way to improve thermoelectric efficiency for these kind of oxides and it has already been applied to ZnO-based materials. The first successful research done in 1996 by Ohtaki et al.[4] for the polycrystalline aluminum doped ZnO of the composition ($Zn_{0.98}Al_{0.02}O$) with high temperature thermoelectric properties. They evaluated the thermal conductivity, electrical conductivity, and Seebeck coefficient at 1000°C. The results of that investigation got the ZT value around 0.65 at 1000°C [5]. During the last decades, several studies of the thermoelectric properties of ZnO doped with either elements such as Al, Ni, Sm, Ce, Dy, Ga and Sb have been reported[1, 2, 19, 20]. Figure 2 shows the number of articles already published between 2009 and 2017.

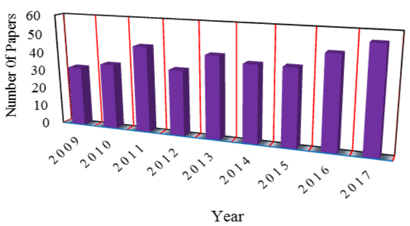

Fig. 2: Number of articles published concerning of zinc oxide dopant based materials.

3. Thermoelectric Properties related with ZnO dopant based materials

In order to obtain a high figure of merit ZT, the thermoelectric materials should possess high Seebeck coefficients and electrical conductivity with low thermal conductivity. A high electrical conductivity is necessary to minimize Joule heating, while a low thermal conductivity helps to retain heat at the junctions and maintain a high temperature gradient [21]. These are the irreconcilable requirements and there are very few materials, which satisfy the above conditions. Among the thermoelectric materials, zinc oxide displays a good seebeck coefficient value, a high thermal stable temperature ranges and low environmental impact [22, 23]. The different investigations on ZnO materials present that their thermoelectric properties can be improved by substitution with different element such as Aluminum[1-4, 24-28], Cerium and Dysprosium[29], Gallium [6, 30-32], Indium[33], praseodymium[34], Antimony[20] and Nickel[7, 19]. Therefore, ZnO as thermoelectric materials is slowly developing, but surely gaining attention as one of the candidates for thermoelectric applications.

Figures 4-7 depicture the temperature dependence of the electrical conductivity, Seebeck coefficient, thermal conductivity and figure of merit for the ZnO materials before and after doping respectively. Figure 4 presents the effect of electrical conductivity percentage changing before and after ZnO doped with Al, Ni, Sm, Ce, Dy, Ga and Sb elements. The results showed that ZnO doped with Al and Ga elements have higher electrical conductivities compared with other elements.

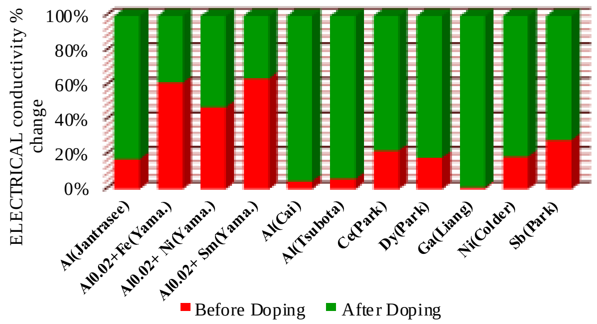

Fig. 4 The effect of electrical conductivity percentage changing with different ZnO doped elements [1-7]

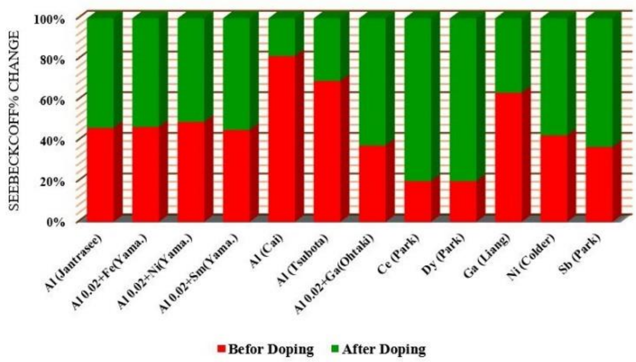

Fig. 5: The effect of Seebeck coefficient percentage changing with different ZnO doped elements [1-7]

The influence of Seebeck coefficient percentage changing before and after ZnO doped with Al, Ni, Sm, Ce, Dy, Ga and Sb elements are shown in Figure 5. From this figure, it was present that ZnO doped with Dy and Ce has higher seebeck coefficient compared with other elements according to different references.

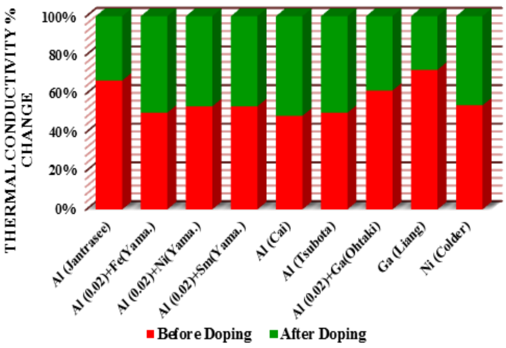

Fig. 6: The effect of thermal conductivity percentage changing with different ZnO doped elements [1-7].

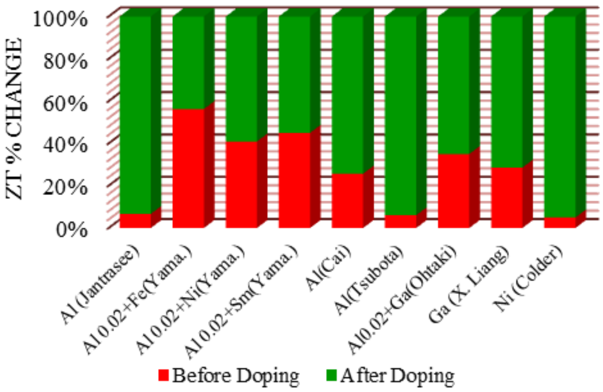

Fig. 7: The effect of figure of merit percentage changing with different ZnO doped elements[1-7]

Figure 6 shows the effect of thermal conductivity percentage changing on the ZnO undoped and doped with different elements such as Al, Ni, Sm, Ce, Dy, Ga and Sb. According to obtain high figure of merit, the thermal conductivity must be lower values. The Figure 6 presents the thermal conductivity of ZnO before and after doping with different elements. From this figure, the lowest thermal conductivity can be obtained from Ga compared to other elements.

Figure 7 shows the figure of merit comparisons between the numbers of references. From this figure, the higher value of that factor can be obtained from Al and Ni elements. According to previous explanations, there are differences in the results obtained from these references. This depends on several factors including bulk density, carrier concentration and grain size ZnO[19].

4. Conclusion

From the detailed literature survey and from the analysis based on this survey, it is found that effective ZnO dopants and kind of doping elements to achieve higher electrical conductivity, lower thermal conductivity and higher carrier concentration of these elements. Therefore, in this paper, a brief research paper on thermoelectric parameters such as electrical conductivity, Seebeck coefficient, thermal conductivity and figure of merit for the ZnO materials before and after doping and their relation with these parameters changing. The effects of certain parameters on the thermoelectric properties of ZnO, have been summarized and presented with short interpretations.

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