# ENHANCING THERMOELECTRIC RESPONCE OF NIO THROUGH NANOSTRUCTURING

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**Abstract** - A large amount of heat wasted in the universe through various sources which can be reused by converting it into electricity through thermoelectric effect. Solid state devices made up of thermoelectric materials are considered as a potential candidate for this waste heat recovery. Currently available thermoelectric materials do not exhibit sufficient efficiency; hence the TE devices are not common in use for general applications. Therefore, the need for developing high-efficiency TE materials for waste-heat-recovery systems is urgent and will bring vast economic and environmental benefits. Despite many decades of efforts, the efficiency denoted by ZT of the commercialized TE materials is still in the range of 1 -2, which limits the wide-scale application of these devices. The material parameters influencing ZT are interdependent which makes it very difficult to manipulate them for enhancing their ZT value. However, some improvements have been observed in ZT, primarily due to a reduction in lattice thermal conductivity. The scattering of phonons by introducing nanostructures in the lattice leads to the improvement in ZT, as the quantum confinement of charge carriers takes place at the nanoscale. Nanostructuring of materials are therefore considered to improve TE efficiency and exhaustive research is being done to develop nanostructured materials with a higher figure of merit. Conventionally, to realize this, heavy elements were used for low thermal conductivity. In general, however, heavy elements are often rare elements, the use of which prevents the industrial application to thermoelectric materials. Recently, the introduction of nanostructures in metal oxides that can reduce the thermal conductivity is expected as a promising approach for the realization of rare-element-free thermoelectric material. The properties of metal oxides are affected by the control over the morphology, structure and size which can be experimentally optimized to obtain desired results for specific application. The present study considers transition metal oxide i. e., Nickel Oxide for studying and improving its TE performance. NiO exists in various oxidation states, it is thermally and chemically stable. So it is durable and suitable for developing as thermoelectric alternative material. We are expecting that this study would paw the path for overcoming the scientific challenges in this field.

**Keywords** - Thermoelectric Properties, Nano Particles, Thermal Conductivity, Electrical Conductivity, Power Factor.

## I. INTRODUCTION

Thermoelectric conversion offers the possibility for waste heat to be reused as electrical energy, which can be developed as an ideal energy source. The issue in this thermoelectric conversion is an insufficient efficiency in the materials [1] – [10].

The energy conversion efficiency of these devices depends on the materials inherent dimensionless parameter known as the figure of merit represented by ZT. The thermoelectric devices made up of materials with $ZT \geq 3$ [11], [12] are supposed to have sufficient efficiency to compete with the conventional energy systems of its range. Presently used TE materials have ZT value is low in the range of 1 to 2 [4], [5]. Hence research is being done to enhance this value. A material to exhibit high ZT value should have high electrical conductivity and simultaneously low thermal conductivity. All kind of conductivities are the phenomenon of carrier transports inside the material which are interconnected. So the suppression of thermal conductivity by any means also results in the reduction in electrical conductivity. As a matter of this fact, the process of enhancing ZT is basically a material trade-off between managing low thermal conductivity along with maintaining high electrical conductivity. To reach ZT a value of 3 or greater is, therefore, seems to be difficult to date. It needs dramatic enhancements in the power factor, which depend on the further reduction in the thermal conductivity and increase of the electron conductivity. With regards to thermal conductivity, any further reduction below the amorphous limit can only occur if one can actively change the group velocity or reduce the number of phonon modes that propagate through lattice.

One of the strategies of achieving this condition is to reduce thermal conduction through phonon scattering. The nanostructuring in the lattice structure changes the phonon scattering in the crystal matrix due to quantum confinement effect, which not only suppresses thermal conductivity but also improves electrical conduction and in turn enhances ZT value of the materials. [13], [14].

The concept of nanostructuring has emerged as a promising approach to high-performance thermoelectric materials in the last two decades [15], [16] and tremendous efforts have been invested in the design of new nanocomposite materials with high figures of merit. The motivation behind the design and implementation of nanostructuring is to take advantage of the reduction in lattice thermal conductivity arising from phonon scattering at grain boundaries and interfaces between the inclusion phase and the matrix.

The present study focuses on developing an alternative material with improved efficiency for thermoelectric applications. We reviewed materials, designs, models, and experimental results reported in the literature and analyzed it to identify the required

properties the material should possess for thermal energy harvesting. On the basis of this review and our earlier studies, we have selected Nickel Oxide to carry out our research on this proposed problem. It is established in the earlier research that transport properties can be optimized by appropriate doping and it also dependent on the density of states [17]. We choose Silver as the dopant for altering the thermoelectric properties of NiO.

We propose to develop thermoelectric properties of Nickel oxide through nanostructuring and doping. The NiO is chemically and thermally stable material and finds a wide range of applications in solar cells [13], electro chromic devices [14], gas sensing[15] to data storage [16]. In bulk form it is insulator but at the nanoscale, it becomes a semiconductor and also the nanostructured NiO allows tuneability in its band gap which makes it a potential candidate for thermoelectric applications. NiO exists in various oxidation states [18], [19] and It is durable with stable chemical properties and optical densities.

The objective here is to prepare nanostructured NiO composite doped with Ag nanoparticles and subsequently determining the effects of varying doping concentrations for enhanced ZT. NiO nanomaterial has been prepared using sol-gel combustion process [20] and samples were obtained by doing Ag nanoparticles in it with various percentage of concentrations. The synthesized samples have been characterized by XRD, LFA and LSR. The analysis of these characterization lead to the study of the TE properties. The properties of this composite are adjusted for developing an alternate TE material with an emphasis on efficiency and affordability.

## II. THERMOELECTRIC MATERIALS

The thermoelectric [TE] materials have an ability to directly convert heat energy into electricity when exposed to the temperature gradient. There are many families of TE materials developed for a wide range of applications targeting different operating temperature ranges.

### 2.1. Thermoelectric Properties

The TE application of a material is based on Seebeck effect and its TE sensitivity is determined by the Seebeck coefficient, generally denoted by "S". It is highly temperature dependent and inherent property of the material. All materials exhibit the TE effect, to some extent. The known materials typically have a Seebeck coefficient between 100 and 1000 µV/K. Metal such as iron has a Seebeck coefficient of around 19 µV/K at $0^{o}$C[21]. Some materials can also have a negative Seebeck coefficient. For example, constantan has a Seebeck coefficient of -35 µV/K at $0^{o}$C. Most metals exhibit Seebeck coefficients of 10 µV/K or less. However, semiconductors have Seebeck coefficients higher than 100 µV/K [22]; therefore, semiconductors are preferred over conductors in thermoelectric modules. Semiconductor TE materials are very popular as they allow tuneability in their band gap so their transport properties can be altered [23], [24].

#### 2.1.1 Figure of Merit

The TE efficiency of a given material is normally measured using a dimensionless quantity ZT known as a figure of merit, defined as:

$$ZT = \frac{S^2\sigma}{k}T \quad \text{..... (1)}$$

Where σ is electrical conductivity, k is thermal conductivity and T is the temperature in Kelvin. A higher ZT value of a TE material implies a higher thermoelectric effect, which usually leads to better performance by a TE device.

#### 2.1.2 Power factor

The electrical conductivity and Seebeck coefficient in Eqn. (1) of a TE material are determined only by its electronic properties; therefore, both these parameters can be combined to define a term called power factor ($P_f$), which is given as:

$$P_f = \sigma S^2 \text{ ..... (2)}$$

It has been observed in studies that the highest power factor $P_f$ occurs at an optimal values of σ and S [34]. This optimization is the basic objective of the present study.

#### 2.1.3 Thermal Conductivity

In addition to electrons and holes transporting heat through TE materials, thermal conduction also occurs by way of elastic vibrations of the lattice, called phonons. Therefore the total thermal conductivity, k, in a TE material comprises of two contributions: (1) heat transportation through carriers: electrons and holes ($k_e$) and (2) phonons moving through the lattice ($k_L$)-

$$k = k_e + k_L \text{..... (3)}$$

Inconsistent with the Wiedmann–Franz law, the electronic thermal conductivity part $k_e$ is directly related to the electrical conductivity and it increases with an increase in carrier concentration-

$$k_e = L\sigma T = L(ne\mu)T \text{ ..... (4)}$$

Where L is the Lorenz factor for free electrons. This transport mode is determined by the elastic scattering of acoustic phonons at lattice defects and the value of $k_L$ depends on the structure, rigidity, atomic masses, and other characteristics of the lattice [36]. In order to improve ZT of a TE material, its $k_L$ needs to be reduced.

#### 2.1.4 Basic Theory for improving ZT

There are broadly three approaches found in the literature for reducing lattice thermal conductivity:

(1) Phonon scattering (2) Complex crystal structures (3) Nanostructuring.

Recently nanostructuring has emerged as a popular strategy for enhancing ZT. At nanoscale quantum confinement effect governs the transport of charge carriers inside the lattices which can effectively influence the lattices thermal conductivity. The thermal conductivity of nanostructures such as superlattices is observed significantly lower than that of their bulk constituent materials [25]. This results in considerable improvement in figure-of-merit in superlattices systems. The concept of superlattices was first introduced by Dresselhaus, Harman, and Venkata Subramanian [26], and since then it has been extensively studied to understand the mechanism for reduction of phonon thermal conductivity through interface scattering [27].

REF -5- The enhancement in ZT value is also possible by chemically adjusting the transport properties of the material. Owing to their transitional characteristics and chemical stability the transition metal oxides are considered to be the promising candidates for such applications. Transition metal oxide exhibit semiconductor properties at nano level and their surface charge density can be increased by doping resulting in conductivity enhancement [28], [29]. Conductivity can also be increased by choosing the appropriate doping material such as alkaline metals, rare earth materials, and transition metals [30].

Nickel oxide, in bulk or nanoscale form, is one of the most efficient materials of this family, for a variety of applications. The nanostructured NiO, because of its large chemical and thermal stability, also shows great promise for use in high temperature and energy conversion applications.

## III. MATERIAL SYNTHESIS

In the present study we are considering Nickel oxide (NiO) nanostructuring and doping it with transition metal Ag for improving TE properties. We propose the tuning in transport properties by doping of Ag in Nickel oxide (NiO) nano-material in appropriate stoichiometric ratio. The properties of the metal oxides are affected by the control of the desired morphology, structure, size and other properties are developed for specific applications [30- 31]. Synthesis process is therefore one of the important factor for size reduction and many synthesis procedures were adopted previously for preparing the doped samples such as chemical evaporation deposition, solid-state synthesis, chemical precipitation and so on [32] – [34]. These methods provide good results but we have considered the sol gel combustion method which has already proven very effective in our earlier work for preparing reduced size materials. The optimization of the precursor concentrations of NiO nanoparticles is done for various doing concentrations of Ag.

## IV. CHARACTERIZATIONS

The X-Ray diffraction, the Laser Flash Analysis (LFA) and LSR [Laser Seebeck and Resistivity] characterization of obtained all the samples have been carried out at thermoelectric lab of BARC [Bhabha Atomic Research Centre] – Mumbai.

### 4.1 X-Ray Powder Diffraction

X - Ray Powder Diffraction has been done for phase analysis using CuKα radiation (λ=1.54Å) on a proto-bench top AXRD system with parameters θ-θ ranging from 15 kV to 35 mA with slit angle variation of 0.5/sec and average crystalline size has been calculated with the help of Debye-Scherer formula.

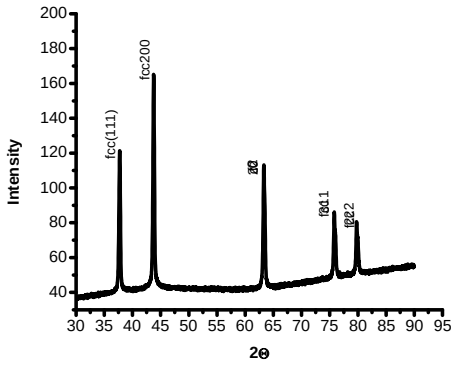



**Fig.1. (a)**

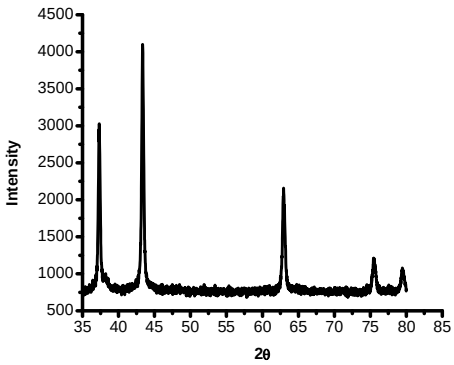



**Fig.1. (b)**

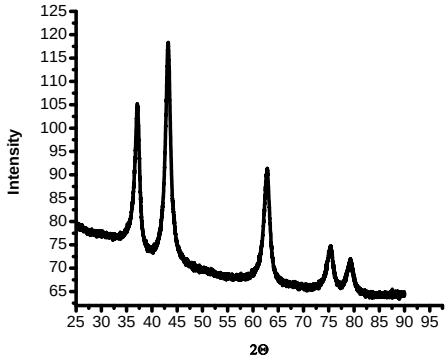



**Fig.1. (c)**

**4.2 Thermoelectric Parameters Characterization:**
Thermal conductivity of the prepared sample has been characterized over the temperature range 900K by Laser Flash Analysis instrument (LFA). Seebeck coefficient and electrical resistivity measurement were done by LSR instrument. All the above parameters are analyzed to calculate TE power and ZT of each sample, and details are presented in Table – 1. The graph plots between respective parameters Vs temperature shown in the Fig. 1 (a, b and c). Than data extracted from the graph has been put in the formula discussed previously in equation (1) for calculating figure of merit ZT of the samples.

**Table1: Thermoelectric Properties of the NiO Samples at T=900K**

| Sample | Doping NiO+Ag Pure + % | k (W/mK) | σ (/μΩm) | S (μV/K) | ZT |
|---|---|---|---|---|---|
| A | P + 0% | 7.06892 | 00 | 1195.24 | 2.67*10^-6 |
| B | P + 2% | 8.786 | 0.0034 | 12.0467 | 5.16*10^-5 |
| C | P + 4% | 13.08 | 0.065 | 19.287 | .00168 |
| D | P + 6% | 41 | 2.52 | 67.63 | .53407 |
| E | P + 8% | 117.65 | 2.65 | 60.3476 | .073 |
| F | P + 10% | 129.098 | 3 | 43.56 | .039 |
| G | P + 20% | 132.376 | 3.74 | 40.067 | .040 |
| H | P + 30% | 138.98 | 3.78 | 23.89 | .014 |
| I | P + 40% | 138.34 | 3.91 | 22.035 | .012 |

## V. RESULTS AND DISCUSSION

The thermoelectric properties obtained by the characterization results of the material are presented in the Table – 1. The TE parameters profile variation with the rise in temperature for pure and doped NiO samples are presented in Figures (1). These X-ray diffraction plots shown in Fig (1) are (a) Pure NiO (b)$Ni_{1-X}Ag_XO$ (X=.004) and (c) $Ni_{1-X}Ag_XO$ (X=.006); the graph analysis explains that the silver doped (4% of .1 mol) & (6% of .1 mol) samples are approximately in pure phase as there is no other impurity peaks found and also the cubic phase while sintered at $600^0$Csamples are prepared supported by the standard JCPDS No.-04-0835 of NiO . In fig 1 it is visible as the sintering temperature increases there is increase in particle size also thus materials are well crystalline because the peaks are so sharp. These plots also indicate that the dopping of Ag and rise in its percentage provides thermal stability to the NiO nanomaterial at the temperature ranging from 900 K to 1000 K. It is clear that the dopping percentage plays an important role in the TE performance of NiO nanomaterial. There is an abrupt rise in the Thermal Conductivity k with the increase of doping percentage beyond 2%, whereas the Electrical conductivity σ rises gradually. At the same time, the Seebeck Coefficient S is highest at the 6% doping. As a result of which the $P_f$ Power Factor and ZT TE Figure of Merit is also highest at 6% Ag doing. The balance between reduction in the k and increase in the σ may occur in this region. This means that the material parameters trade-off can be achieved in NiO nanomaterial for 6% of Ag doping. The sample D with 6% Ag doing exhibits TE figure of merit ZT= 0.534 at T=$600^o$K 300 times higher than sample C with 4% and about 8 times higher than sample E with 8% of doping.

## CONCLUSIONS

The transition metal oxide nanomaterial NiO appears to possess very interesting TE properties. Doping of Ag nanoparticles further improves its TE response. An elaborate investigation of TE properties of Ag doped NiO material in the range of 6% doing at T= K can unfold the hidden potential of NiO to be developed for TE applications. The similar studies on NiO with other dopants for various doping percentages are needed. NiO is a potential alternative for presently commercially used thermoelectric material. We are expecting this study would paw the path for overcoming the scientific challenges in this field.

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