Analysis of Thermoelectric parameters of silver doped NiO nanoparticles

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Abstract: Alteration in thermoelectric properties of any specific materials by doping is one of the effective and popular routes. We report the experimental results followed by the mathematical calculations aimed at developing effective thermoelectric materials for high temperature applications. Transition metal oxide materials are the promising candidates for renewable energy due to their chemical stability. Nickel oxide (NiO) one of the most efficient materials of this family, it has wide range of applications such as gas sensing devices, smart windows & solar cell etc. it can also be used in high temperature applications. Transition metal oxide at nano level exhibit semiconductor properties and by doping the conductivity can be enhanced due to increase in surface charge density. Conductivity can also be increase by choosing the appropriate doping material such as alkaline metals, rare earth materials and transition metals such as: Ag. So we propose tuning in transport properties by appropriate doping in Nickel oxide (NiO) nano-material in stoichiometric ratio.

Synthesis process is one of the important factor for size reduction thus we can choose the sol gel method for synthesize the NiO with various doping concentration. This method is very effective to prepare reduced size material. These results analyze by the X-Ray diffraction, other transport properties analyze by the Linsis made Seebeck and resistivity measurement system, Laser flash analysis (LFA) in Thermoelectric lab, BARC. This shows the change in seebeck coefficient, thermal conductivity of Nickel oxide due to silver doping. By this doping surface charge density increases so the photo conductivity increases and thus the electrical conductivity also increases without much affecting thermal conductivity and if the electrical conductivity increases this improves the value of power factor automatically and hence the thermoelectric figure of merit increases.

Keywords; Nickel oxide, Seebeck coefficient, electrical resistivity, thermal conductivity.

1. Introduction

Energy is the continuous and demanding need of human race. Many conventional and artificial sources are being used by the society. But this continuous need demands enormous energy at low cost which could be possible by the use of waste energy efficiently; solar energy. Solar energy is the only energy which could be exploiting either of the way or in large amount also or we can say that unlimited amount. Only the need is we make a kind of device made with a specific material which converts this energy in useful work. Many researchers give an idea of material that converts this solar energy in to work like Si, Ge semiconductor material with different doping and doping concentration, Bi_2Te_3, $SrTiO_3$ and so many materials are there for such applications.[1-3] In the above series oxides materials are consider to be less used materials, so we have select the NiO for our work to analyze its thermal conductivity, Seebeck coefficient and figure of merit in low dimensions and also optimized the above parameters by doping with Silver and Lithium in comparison with the pure Nickel oxide. Lithium doping is already being done by the W. Shin & N. Murayama *et al* in his paper they reported ZT= .75^x 10^{-4}. [4] So many researchers have been done in this view and it is concluded that transport properties are optimized by appropriate doping and it also dependent on density of states [5].Hence in place of Lithium we choose Silver as dopant for altering the thermoelectric properties of NiO.

Many synthesis procedures were adopted previously for preparing the doped samples such as chemical evaporation, solid state synthesis, chemical precipitation and so on [6-9]. These methods provide the good results. But one of the most effective methods has been discussed by us in this paper [10]. The only uniqueness is the use of reagent. We use tartaric acid in this method. The prepared sample has been characterized by various techniques such as; for phase analysis X-ray diffractrometer is used [11-12] morphological analysis can be done by SEM & EDAX [13-14] Thermal conductivity is measured by Laser Flash Analysis (LFA) Seebeck coefficient is measured by LSR. After measuring the above properties *ZT* is calculated with the help of formula:

$$ZT= (S^2 \sigma/k)\ T \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. \text{(i)}$$

Where Z is the figure of merit at absolute temperature, S is the seebeck coefficient, σ is the electrical conductivity and k is the thermal conductivity. [15] In this work we have analyze all the above parameters of all samples qualitatively for high temperature applications.

2. Experimental details

2.1 Synthesis

Synthesis of NiO and NiO-Ag by sol-gel combustion process:

Preparation of pure NiO (sample N-1)- Nickel Nitrate hexa hydrate[$Ni(NO_3)_3$*$6H_2O$] precursor has been taken for the synthesis and methanol is used as solvent, tartaric acid [$C_4H_6O_6$]was act as the acidic reagent and ethylene glycol used as a capping agent for better desirable results.0.1 mole solution is prepared. The whole mixture was air dried at 180^0C for 12 hrs and then dried mixtures were calcined at 400^0C for 2 hrs. During the calcination combustion process take place by which the nickel nitrate converted in to nickel oxide. Black colored sample has been crushed properly and then pellets of the sample were formed by applying about 10 tons of weight. These pallets now placed in the furnace for sintering at the temperature 600^0c for strengthen the samples. These pallets now subjected to the characterization process. The reactions were take place as follows:

$Ni\ (NO_3)_2{*}6H_2O{+}.1C_4H_6O_6{=}\ NiO{+}3HNO_3{+}.4CO_2{+}4.8H_2O$………………………………… (ii)

For silver doped NiO(Sample N-2 and Sample N-3)- Nickel Nitrate hexa hydrate [$Ni(NO_3)_3$*$6H_2O$] and Silver Nitrate[$AgNO_3$] precursor has been taken for the synthesis and methanol is used as solvent, tartaric acid [$C_4H_6O_6$]was act as the acidic reagent and ethylene glycol used as a capping agent for better desirable results.0.1 mole solution is prepared. In sample N-2 doping of silver nitrate is 4% with 96 % of Nickel Nitrate [$Ni(NO_3)_3$*$6H_2O$] with respect to 0.1 mole of solution and in sample N-3 doping of silver nitrate is 6 % with 94 % of Nickel Nitrate [$Ni(NO_3)_3$*$6H_2O$] with respect to 0.1 mole of solution. Rests process same as describe for the pure NiO [Sample N-1] sample. Reaction takes place as follows:

$Ni\ (NO_3)_2{*}6H_2O{+}AgNO3{+}.2C_4H_6O_6{=}\ NiAgO{+}4HNO_3{+}.8CO_2{+}4.6H_2O$…………………… (iii)

2.2 Characterizations

2.2.1 X-ray powder diffraction

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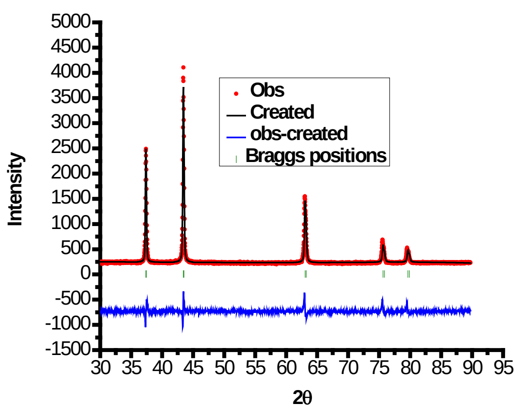
All freshly prepared pellets were characterized by x ray powder diffraction for phase analysis using CuKα radiation (λ=1.54Å) on an proto-bench top AXRD system with parameters θ-θ ranging X-ray input 15 kV and 35 mA with slit angle variation .5/sec and average crystalline size has been calculated with the help of Debye-Scherer formula. Rietveld refinement also done by the full proof suit-64 bit.

2.2.2 Thermoelectric parameters characterization:

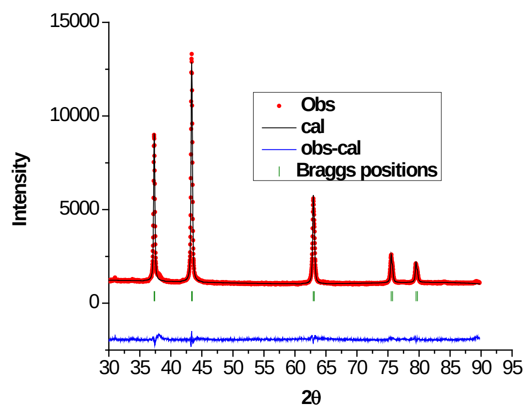
Thermal conductivity of the prepared sample has been characterized over the temperature range 900K by Laser Flash Analysis instrument (LFA). Seebeck coefficient and electrical resistivity measurement has been done by LSR instrument. All the above parameters analyzed by plotting graph between respective parameter Vs temperature. Than data extracted from the graph has been put in the formula discussed previously for calculating figure of merit of the material.

3. Results and discussion

3.1 For X-ray diffraction plot of (a) Sample N-1 (b) Sample N-2 (c) Sample N-3; the graph analysis explains that the silver doped samples are approximately pure phase as there is no other impurity peaks found and also the cubic phase while sintered at 600^0C samples 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. In this paper we only discussed the rietveld parameters of silver doped nickel oxide samples, although pure nickel oxide also prepared by the same method but only comparative study has been done with pure nickel oxide data. In table.1 we discussed the rietveld parameters and table to describe the average crystalline size of the particle prepared by sol-gel method. For rietveld refinement Space group of the NiO is 225(F m 3 m) and cubic Structure has been taken.



(a)



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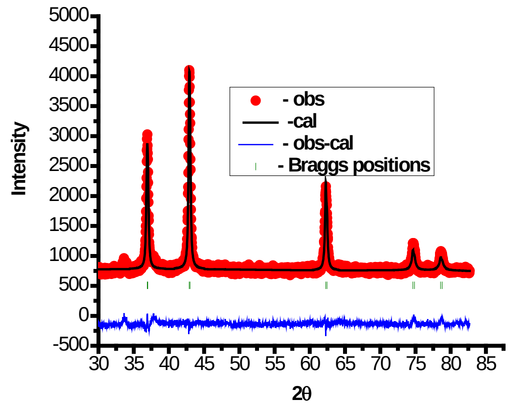

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Fig. 1. Rietveld refinement of (a) sample N-1 (b) Sample N-2 (c) sample N-3

Table: 1
Rietveld Refinement structural parameters of Pure NiO and silver doped NiO nanoparticles.

S.No	**MATERIAL**	**U**	**V**	**W**	**a=b=c**	**occupancy**	**GOF**	**Chi^2**
1	sample N-1	.053908	.047862	.0067260	4.166	Ni=.9560, O-1.0051	1.285	1.66
2	sample N-2	-.04740	.0868	.0231	4.172	Ni=.9239, O=.94687	1.14	1.30
3	sample N-3	1.360	-1.447	.4292	4.21	Ni= .9945, O=1.0018	1.238	1.53

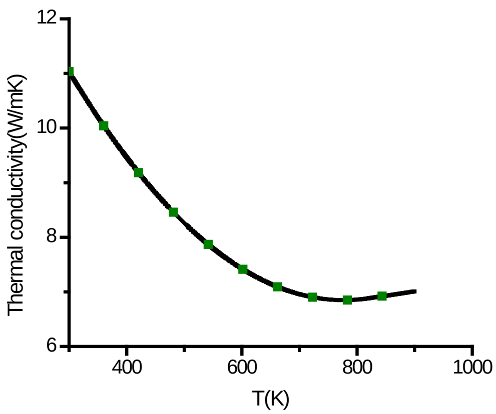
Table: 2 Average crystalline size of sample N-1 ,sample N-2 and sample N-3

2θ(degree)			Θ (radian)			FWHM			β(radian)			Crystalline size (nm)		
sample N-1	sample N-2	sample N-3	sample N-1	sample N-2	sample N-3	sample N-1	sample N-2	sample N-3	sample N-1	sample N-2	sample N-3	sample N-1	sample N-2	sample N-3
37.20	36.9	37.33	.32	.315	.32	.37	.338	.4112	.0064	.0058	.00717	21.6	20	19.01
43.25	43.3	43.36	.37	.368	.37	.69	.338	.39	.012	.0058	.0068	11.55	20	19.8
62.85	62.5	62.93	.54	.534	.54	.48	.438	.53	.0083	.0076	.0092	16.7	19.01	15
75.36		75.43	.65		.65	.69			.012			11.55		
79.39		79.45	.69		.69	1.08			.018			7.7		
Average crystalline size: -	NiO≈ 14 nm ,NiAgO (Ag=.004)≈20 nm , NiAgO (Ag=.006)≈18 nm													

3.2 Thermal conductivity

Fig. 2. represents Thermal conductivity Vs temperature plot of (a) sample N-1 (b) sample N-2 (c) sample N-3. Sample N-1 shows the reduction in thermal conductivity with temperture while other sample N-2 and sample N-3 shows the increase in thermal conductivity linearly with temparature upto 900K around 41 Wm/K. Thermal conductivity is incresed due to the contribution of electron is more

than that of the phonons because silver doesnot replace the Ni atoms as the other metal ions but it has tendancy to accumalete across the grain boundries so that the electronic contribution increases as compare to the phonons. [16] But if we analyze the sample N-2 after 650K thermal conductivity starte decreasing up to 900K . This reduction in thermal conductivity after certain temperature is occur due to thermal hyestrisis in the material.[17]while sample N-3 shows linear increment in thermal conductivity with temperature.



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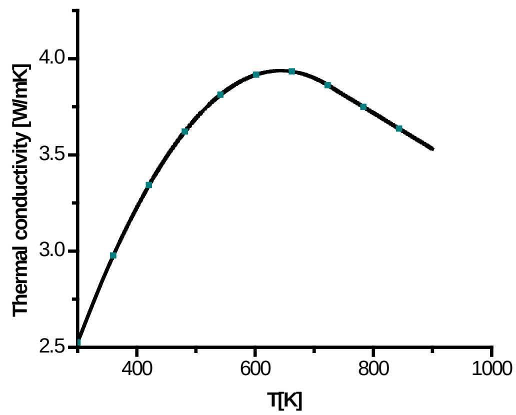

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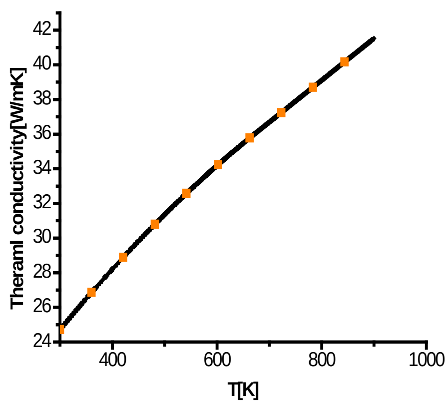

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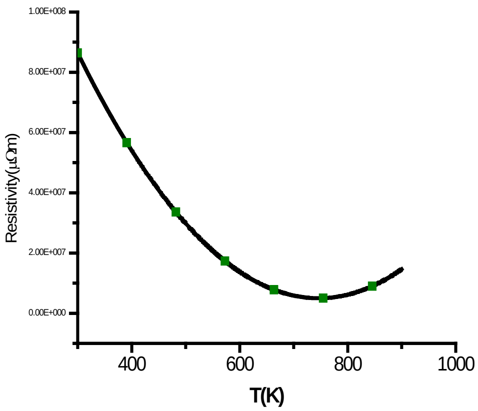
Fig. 2 Thermal conductivity Vs temperature plot of (a) sample N-1 (b) sample N-2 (c) sample N-3

3.3 Electrical Resistivity

Fig.3 represents the electrical resistivity Vs temperature plot of (a) sample N-1 (b) sample N-2 (c) sample N-3. By analyzing the electrical resistivity curves of sample N-1, Sample N-2 & sample N-3 it is concluded that the sample N-1 and sample N-3 shows the gradual decrement in resistivity with temperature but sample N-2 shows increment in electrical resistivity up to 900K. Although the resistivity of the sample N-2 is very much less than the Sample N-1 but it shows increment with temperature in the curve . It is remarkable that as soon as we doped silver in NiO in certain amount (6%) its resistivity decreases due to inclusion of metal ions on the grain boundaries of the material which enhances the conductivity of the material. [18] In sample N-2 the resistivity increases due to charge carriers present in the system interact with the lattice but further increase in temperature reduced the resistivity because of increases concentration of majority charge carriers. [19]



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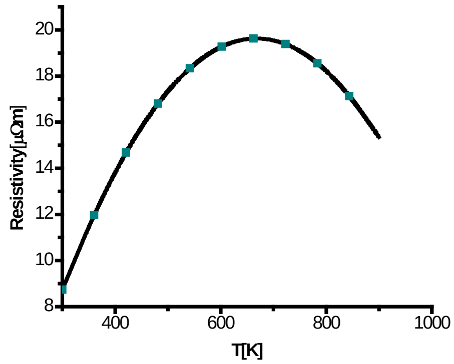

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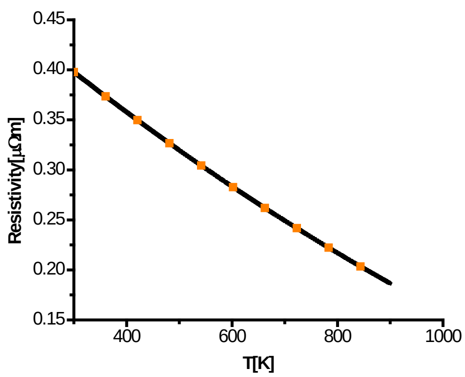

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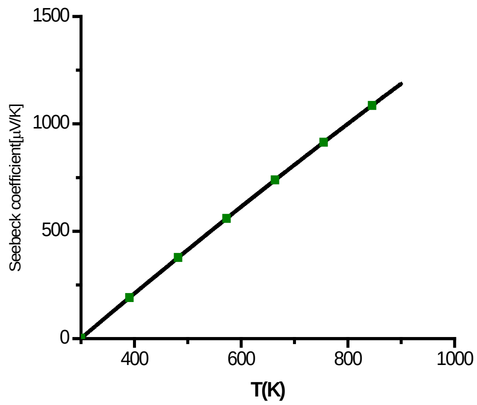
Fig.3. Electrical resistivity Vs temperature plot of (a) sample N-1 (b) sample N-2 (c) sample N-3

3.4 Seebeck coefficient

Fig.4. Depicted Seebeck coefficient Vs temperature plot of (a) sample N-1 (b) sample N-2 (c) sample N-3. These graphs show the temperature dependency of Seebeck coefficient. Sample N-1 shows the high Seebeck coefficient and also the linear increment with temperature but in graph (b) sample N-2 initially Seebeck coefficient increases from room temperature to 800K after this temperature it started decreases up to 900 K this change occur due to thermal hysteresis quoted in the thermal conductivity analysis. On the other hand graph (c) sample N-3 shows the initial decrement in Seebeck coefficient upto temperature 580K due to increased metallic concentration which enhance the electronic component of thermal conductivity between high to low temperature but after this temperature thermo-power increases upto 900K because due to electron and hole concentration become equal which reduces the mobility so the seebeck coefficient increases. [20-22] both the samples shows the different characteristics due to doping concentration variation. Thus the Seebeck coefficient is depending upon the doping concentration.



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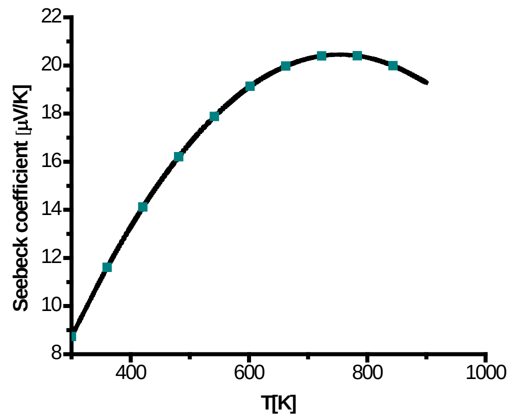

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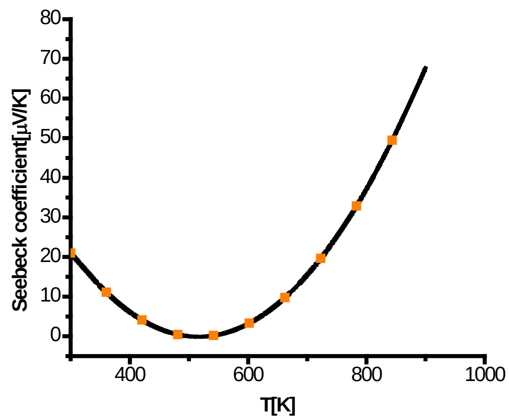

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Fig.4. Seebeck coefficient Vs temperature plot of (a) sample N-1 (b) sample N-2 (c) sample N-3

3.5 Figure of Merit:

Fig. 5. Shows the figure of merit Vs temperature plot of (a) sample N-1 (b) sample N-3 (c) sample N-3 both the plots depict the value of figure of merit (ZT) at different temperatures. Sample N-1 has ZT= $2.67*10^{-5}$ which is very less and not significant for any energy applications after doping Sample N-2 shows ZT= .001 at 300K and at 900 K the value of ZT=.006 which is less as compare to other doped reported data. [4] But if we analyze the value of figure of merit of sample N-3 at the given temperature range it gives significant increment in ZT as at 300K ZT of sample N-3 is ZT=.013 and at 900K ZT = .53. Thus the sample N-3 is the better candidate for the thermoelectric applications.

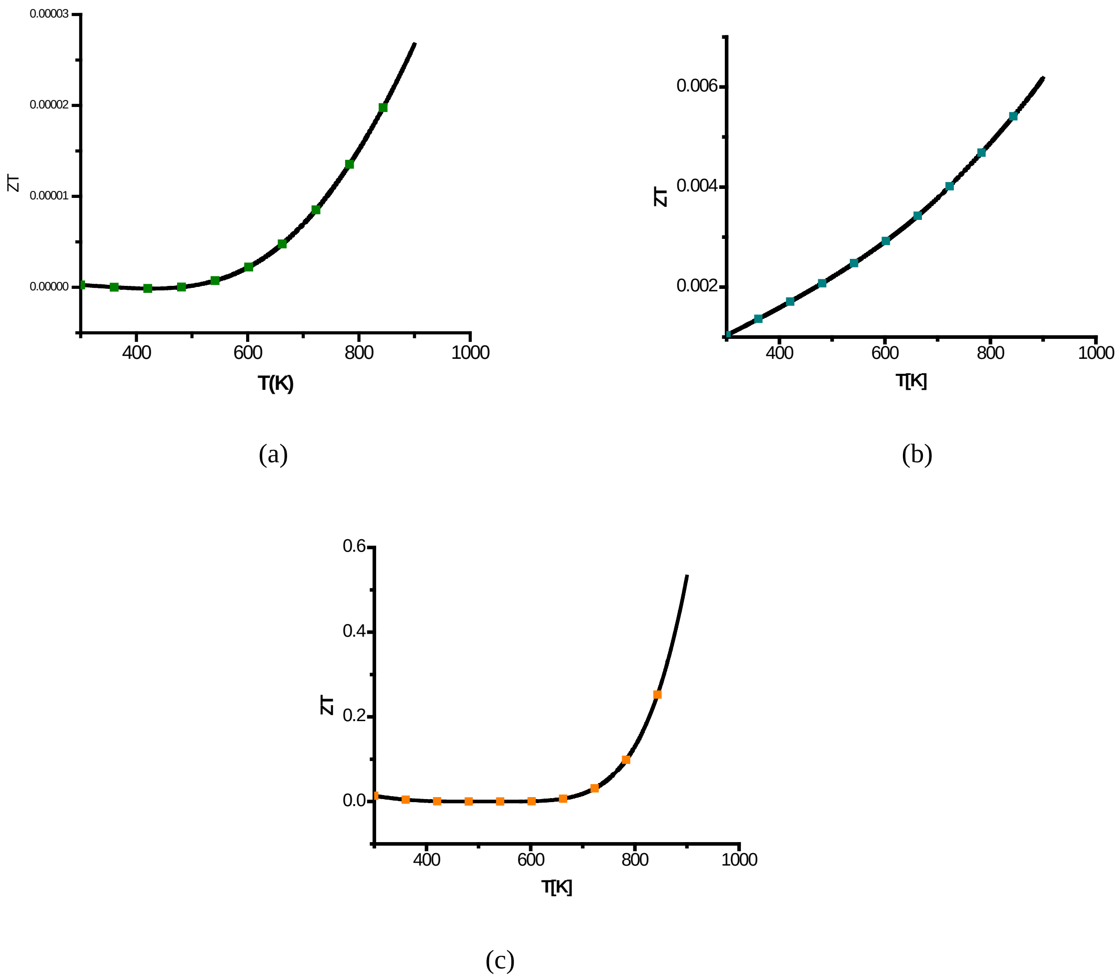

Fig.5. ZT Vs temperature plot of (a) sample N-1 (b) sample N-2 (c) sample N-3

4. Conclusion

The following research concluded that we can enhance the thermoelectric figure of merit of the material with reducing size and doping concentration variation also. This paper also help full to describes the synthesis method for reduced size or Nanoscale material synthesis specially meant for thermoelectric applications. There is wide scope of the alteration in transport property of transition metal oxide nanostructures material using for high temperature applications. Silver doping gives the better results in enhancement of thermoelectric figure of merit of NiO nanoparticles. But the figure of merit also depend on the doping concentration as we found highest figure of merit value **≈.53** at 900 K in sample N-3. Although the seebeck coefficient of sample N-1 is much better than that of sample N-2 and sample N-3 but it could not provide the significant value of figure of merit (ZT) which is essential requirement for the thermoelectric applications. Thus by the specific amount of doping we can improve the figure of merit of the NiO so that it can be an option for low cost high stability thermoelectric material.

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References

[1] C. M. Bhandari , D. M. Rowe, Silicon–germanium alloys as high-temperature thermoelectric materials, Journal Contemporary Physics, 21(2006)219-242

[2] K. Romanjek , S. Vesin ,L. Aixala , T.Baffie , G. Bernard-Granger , J.Dufourcq , High-Performance Silicon–Germanium-Based Thermoelectric Modules for Gas Exhaust Energy Scavenging J. Electro Mater 44(2015) 2192–2202

[3]Z. Lu , H. Zhang ,W. Lei , D.C.Sinclair ,I. M. Reaney , High-Figure-of-Merit Thermoelectric La-Doped A-Site-Deficient $SrTiO_3$Ceramics ,Chem. Mater. 28 (2016) 925-935

[4] W. Shin, N. Murayama, Li-doped nickel oxide as a thermoelectric material,Jpn J of appl phys 38(11B) (1999) 336 -339

[5] G. Ren,J.Lan,C.Zeng,Y.Liud, B.Zhan, S.Butt Y.H. Lin and C.W.Nan, High Performance Oxides-Based Thermoelectric Materials,JOM 67(2015)211-221

[6] M. D. Irwin , D. B. Buchholz , A. W. Hains , R. P. H. Chang, T.J. Marks , *p*-Type semiconducting nickel oxide as an efficiency-enhancing anode interfacial layer in polymer bulk-heterojunction solar cells**,**PNAS,105 (2008)2783-2787

[7] Z. Huang, G. Natu , Z. Ji , P. Hasin , Y. Wu , p-Type Dye-Sensitized NiO Solar Cells: A Study by Electrochemical Impedance Spectroscopy ,J. Phys. Chem. C, 115(2011)25109-25114

[8] H. Tian , B. Xu ,H. Hong Chen, E .M.J. Johansson, G. Boschloo , Solid-state perovskite-sensitized p-type mesoporous nickel oxide solar cells ChemSusChem. in Willey Online Library 7(2014)2150-2153

[9] V. Mathur , K.S. Rathore , K. Sharma , Evaluation of Energy Band Gap, Thermal Conductivity, Phase Transition Temperature and Elastic Response of PS/CdS Semiconducting Optical Nanocomposite, World Journal of Nano Science and Engineering,3 (2013)93-99

[10] M.M. Ba-Abbad , P.V. Chai, M.S. Takriff , A. Benamor, A. W. Mohammad, Optimization of nickel oxide nanoparticle synthesis through the sol-gel method using Box-Behnken design,Mater. Des. 86(2015)948-956

[11] P. Saravanan , R. Gopalan, V. Chandrasekaran , Synthesis and Characterisation of Nanomaterials**,** Defence Science Journal-DRDO,28(2008)504-516

[12] R. Sharma, D.P. Bisen, U. Shukla, B. G. Sharma, X-ray diffraction: a powerful method of characterizing nanomaterials, Recent Res.Sci.Tech,4(2012)77-79

[13] M. Kooti, M. Jorfi, Synthesis and characterization of nanosized NiO_2 and NiO using Triton® X-100,Cent. Eur. J. Chem.,7(2009)155-158

[14] G. S. Harish,C. S. Reddy , P.S. Reddy, B. R. Reddy, Synthesis and characterization of Cu doped NiO nanoparticles ,IJMER4 (2014)62-68

[15] G.J. Snyder, E.S.Toberer , Complex thermoelectric materials,Nat Mater7 (2008)105-114

[16] R. Sharma, K. Yadav K. Effect of lattice defects on the structural and optical properties of $Ni_{1-X}Ag_XO$ (where $X = 0.0$, 0.01, 0.03, 0.05, 0.10 and 0.15) nanoparticles,Appl Phys A 124 (2018)88-92

[17] H. Iwasaki, Thermal hysteresis behaviors of thermoelectric properties,Jpn J. Appl Phys 53(2014)125502

[18] D. Srivastava , C. Norman , F. Azough , M.C.Sch€afe ,E. Guilmeau , R. Freer R. , Improving the thermoelectric properties of SrTiO3-based ceramics with metallic inclusions,J. Alloys Compd 731 (2018) 723-730

[19] K. Conder , Electronic and ionic conductivity in metal oxides, Laboratory for Developments and Methods, Paul Scherrer Institute, 5232 Villigen PSI

[20] L. Xu , Y. Liu , B. Chen ,C. Zhao, K. Lu, Enhancement in Thermoelectric Properties Using a P-type and N-type Thin-Film Device Structure , Polym Compos 10 (2013)1728-1734

[21] Y. Liu , D. Cadavid , M. Ibáñez , S. Ortega, S. Martí-Sánchez , O. Dobrozhan ,V. Maksym ,M. V. Kovalenko , J. Arbiol , A. Cabot A., Thermoelectric properties of semiconductor-metal composites produced by particle blending ,APL Mater 4, (2016)1-12

[22] A. Shaheen , W. Zia, M.S. Anwar , Band Structure and Electrical Conductivity in Semiconductors, LUMS School of Science and Engineering 10 (2010)1-55

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