

# Theoretical Study of Lattice Thermal Conduction in SrTiO<sub>3</sub>/BaTiO<sub>3</sub> Superlattice Nanowires

Yashwant Singh Chandel<sup>1</sup>, Purnima Swarup Khare<sup>2</sup>

<sup>1,2</sup>Rajeev Gandhi Technical University, Department of Applied Physics, Airport road, Gandhi Nagar, Bhopal, India

**Abstract:** In this paper, environmental friendly materials: thermoelectric oxides are chosen as research directions, and the perovskite oxide SrTiO<sub>3</sub> based superlattice is selected as a material system for thermoelectric power generation. Combined with diffuse interface boundary conditions Boltzmann transport equation based on diffuse mismatch model is used to calculate thermal conductivities of SrTiO<sub>3</sub>/BaTiO<sub>3</sub> nanowires. The thermal conductivities of SrTiO<sub>3</sub>/BaTiO<sub>3</sub> nanowires with length segments of 5 nm each having diameters of samples 0.44 nm, 0.55nm, 0.75 nm, 1.18 nm and 1.58 nm were measured at room temperature and the thermal conductivities of SrTiO<sub>3</sub>/BaTiO<sub>3</sub> nanowires samples with the diameters of 5 nm each, having equal length segments of 16 nm, 21 nm, 33 nm, 45 nm and 57 nm were measured at room temperature. Reduced effective thermal conductivity of superlattice nanowire was found to be 0.5 W/mK for  $d_w = 0.44$  nm and  $L = 5$  nm. The obtained conclusion suggests the idea that SrTiO<sub>3</sub>/BaTiO<sub>3</sub> superlattice nanowire can be a very good candidate for thermoelectric performance by reducing the periodic length and the wire cross-sectional width. Finally we also concluded that the thermal conductivity of the nanowire reduce more effectively due to reduction in diameter of nanowire in comparison to reduction in its periodic length.

**Keywords:** Superlattices (SL), phonon interface scattering, phonon boundary scattering, quantum dots, thermoelectrics. Boltzmann transport equation, diffuse mismatch model

## 1. Introduction

The emerging global need for energy production, sustainable development of eco-friendly thermoelectric materials are expected which widely used in power generation from the waste heat from automobiles etc. Thermoelectric modules are the devices that directly convert thermal energy into electrical energy without emitting greenhouse gases. This effect of converting thermal energy into electric energy is called "Seebeck effect". [1] Seebeck effect refers to a phenomenon in which a temperature difference creates an electric potential. So for the power generation highly efficient thermoelectric materials are needed. [2]

The efficiency of thermoelectric devices can be measured by the figure of merit  $ZT$  which is a dimensionless quantity given as  $ZT = S^2\sigma T/\kappa$ , where  $S$  is the Seebeck coefficient,  $\sigma$  is the electrical conductivity,  $T$  is the absolute temperature and  $\kappa$  is the total thermal conductivity (i.e. lattice and electrical thermal conductivity). Therefore to improve the figure of merit of thermoelectric materials high PF value and a low lattice thermal conductivity are needed. [3, 4]. Performance of thermoelectric materials can be improved by using low-dimensional and superlattice structured thermoelectric materials. Lattice thermal conductivity can be reduced by using this approach of nanostructures and superlattice thermoelectric materials. [5] These thermoelectric materials are of great interest due to low size, cheaper than bulk materials. [6] which results in being improve the efficiency of thermoelectric devices. The reduction in lattice thermal conductivity in nanostructured thermoelectric materials is due boundary scattering of phonons when the size of thermoelectric materials is comparable to phonon mean free path. [7]

Semiconductors are the efficient thermoelectric materials due to their lower thermal conductivity than bulk materials as the

phonons behavior in semiconductors reduce the thermal conductivity when their diameters are comparable to the phonons mean free path. [8, 9] On the other hand superlattice structure with Nano scale size is also shows low lattice thermal conductivity. [3, 8, 10] Therefore semiconductor based superlattice nanowires are of great interest to improve the performance of thermoelectric materials due to their better interface and boundary scattering of phonons. [8]

Many previous researches have been attempting to investigate the transport properties in superlattice structures which results in reduction of the lattice thermal conductivity. In previous paper [6], the thermoelectric quantum dot semiconductor superlattices Bi<sub>2</sub>Te<sub>3</sub>/Sb<sub>2</sub>Se<sub>3</sub> and PbTe/PbTeSe shows improved thermoelectric properties along the cross plane and in-plane direction. Moreover, p-type LSMO/LMO superlattice material results lower thermal conductivity 0.89 W/mK in cross-plane direction at the room temperature which is lower than the thermal conductivities of bulk oxide thermoelectric materials. [11] The reduced thermal conductivity of Si/Si<sub>x</sub>Ge<sub>1-x</sub> ( $0 < x < 1$ ) superlattice nanowires were reported due to the phonon scattering and thus reduction in the phonon contribution in the thermal conduction. The figure of merit thus improves due to low thermal conductivity. [12] In other research paper, [13] lower thermal conductivity of Si/SiGe superlattice nanowires than the bulk Si nanowires of similar diameters were also reported.

In the present study we investigate the thermal conductivity of perovskite oxides SrTiO<sub>3</sub> and BaTiO<sub>3</sub> based superlattice nanowire as potential candidate for thermoelectric applications. We expect a lower thermal conductivity than bulk oxides which improve the figure of merit  $ZT$  of thermoelectric materials.

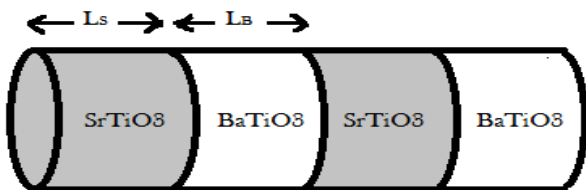
SrTiO<sub>3</sub> is a potential thermoelectric oxide because of eco-friendly nature, non-toxic and stable at very high temperature. But the bulk SrTiO<sub>3</sub> has very large thermal conductivity of ~12 W/mK at room temperature. [14]

For the reduction of thermal conductivity of SrTiO<sub>3</sub>, doping and Nano structuring are done. The reduced thermal conductivity could be observed in SrTiO<sub>3</sub> nanowires due to interface and boundary scattering. [15]

Barium titanate (BaTiO<sub>3</sub>) is a potential candidate of thermoelectric materials widely used for electronic devices, when it assumes the tetragonal structure.[16] Due to its largest lattice constant, it has largest ZT value among SrTiO<sub>3</sub>, BaTiO<sub>3</sub> and CaTiO<sub>3</sub> [17]. Bulk BaTiO<sub>3</sub> has low thermal conductivity of 2.65 W/mK hence suitable for thermoelectric applications. [18] In this research paper, Boltzmann transport equation with diffuse mismatch interface conditions are used to study the transport properties of phonons assuming the scattering of phonons in superlattice nanowire of semiconductor oxide SrTiO<sub>3</sub>/BaTiO<sub>3</sub> at room temperature. The lattice thermal conductivity of SrTiO<sub>3</sub>/BaTiO<sub>3</sub> superlattice nanowire at room temperature are calculated by putting the parameters such as phonon mean free path and thermal conductivity of bulk materials at room temperature in Boltzmann transport equation (BTE) of phonons with diffuse mismatch model (DMM) interface conditions. In this paper, we first introduce the theoretical background of thermal conductivity, the simulation details, and at last results and discussion.

## 2. Theoretical Background of Thermal Conductivity

Thermal conductivity can be calculated by solving the Boltzmann transport equation.[19] Boltzmann transport equation based on diffuse mismatch model with diffuse interface boundary conditions is the fundamental equation for the theoretical study of the diffusive boundary and interface scattering of phonons in the materials ignoring its electrical transport properties.[20] Superlattice structure of nanowire is formed when two different nanodots say *S* and *B* are arranged alternately having its periodic length of  $L=L_S+L_B$ . In this superlattice nanowire, completely diffusive and elastic scattering between the interfaces of two different materials which causes interfacial transport of phonons predicted by Boltzmann transport equation (BTE) based on Diffuse Mismatch Model (DMM).[21]



**Figure 1:** The alternately arranged SrTiO<sub>3</sub> and BaTiO<sub>3</sub> nanodots forming superlattice structured nanowire in which  $L_S$  and  $L_B$  represent the length of SrTiO<sub>3</sub> and BaTiO<sub>3</sub>

## 3. Simulation Details

The diffuse mismatch model is the low temperatures model which assumes linear phonon dispersion relation with a constant phonon velocity typically applied at temperatures lower than Debye temperature. The Debye temperatures for the thermoelectric materials taken in this work are 486 K for BaTiO<sub>3</sub> [22] and 513K for SrTiO<sub>3</sub> [15]. We therefore assume that for both materials, the diffuse mismatch model is applicable at room temperature. [21]

The lattice thermal conductivity  $k_{SL}$  of superlattice nanowires for the diffusive boundary scattering of phonons, is calculated by the equation given by [23],

$$\left(\frac{1}{C_S v_S \tau_{SB}} + \frac{1}{C_B v_B \tau_{BS}}\right) \left(1 + \frac{\tau_{SB} + \tau_{BS}}{2}\right) + \frac{3}{D_w} \left(\frac{L}{k_{SL}} = \frac{L_S}{k_S} + \frac{L_B}{k_B} + 4\right) \quad (1)$$

where  $k$ ,  $v$  and  $C$  are the lattice thermal conductivity, phonon group velocity and volumetric specific heat capacity of the bulk material (*S* or *B*),  $\tau_{SB}$  (or  $\tau_{BS}$ ) is the transmission probability of energy of phonons from *S* to *B* or from *B* to *S*, through the interface of SrTiO<sub>3</sub> and BaTiO<sub>3</sub>.  $\alpha_S$  (or  $\alpha_B$ ) is a geometric factor which is given by [24],

$$\alpha = \frac{N^S - N}{N^S [\ln\left(\frac{2L_S \text{ or } B}{ND_w}\right) + 0.5]} \quad (2)$$

where  $N$  is the number of segments of nanowire,  $L_{S \text{ or } B}$  is the length segment of nanowire,  $D_w$  is the nanowire diameter. It only depends on the aspect ratio  $L_S/D_w$  (or  $L_B/D_w$ ) of the nanodots *S* and *B*, its values lie between 0.75 and 1 for cylindrical wires. In Equation (1), phonons scattering in pure bulk materials is shown by first and second term of the equation, third term accounts for the interface scattering and fourth term shows the boundary scattering in nanowire. These terms contribute for the lattice thermal conductivity of super lattice nanowire. The transmission probability using the diffuse mismatch model,  $\tau_{SB}$  is given by

$$\tau_{SB} = \frac{C_B v_B}{C_S v_S + C_B v_B} \quad (3)$$

and  $\tau_{BS} = 1 - \tau_{SB}$ .

Equation (1) can then be rearranged as

$$\frac{L}{k_{SL}} = \frac{L_S}{k_S} \left(1 + \frac{4\Delta_S}{3L_S} + \frac{\Delta_S}{\alpha_S D_w}\right) + \frac{L_B}{k_B} \left(1 + \frac{4\Delta_B}{3L_B} + \frac{\Delta_B}{\alpha_B D_w}\right) \quad (4)$$

Where  $\Delta_S$  and  $\Delta_B$  are the phonons mean free path in bulk materials *S* and *B* respectively, which are derived from kinetic theory, [1, 2]

$$k = \frac{1}{3} C v \Delta \quad (5)$$

Where  $k$  is the thermal conductivity,  $v$  is the group velocity of phonons,  $C$  is the volumetric heat capacity, and  $\Delta$  is the mean free path of the phonons.

The effective phonon mean free path  $\Delta_{eff}$  for one segment (say *S* or *B*) in the superlattice nanowire is given by

$$\Delta_{S,eff}^{-1} = \Delta_S^{-1} + \frac{4}{3L_S} + \frac{1}{\alpha_S D_w} \quad (6)$$

The effective thermal conductivity  $k_{eff}$  in each segment is given by,

$$k_{S,eff} = (\Delta_{S,eff} / \Delta_S) k_S \quad (7)$$

Final expression of the lattice thermal conductivity  $k_{SL}$  of superlattice nanowire in terms of effective thermal

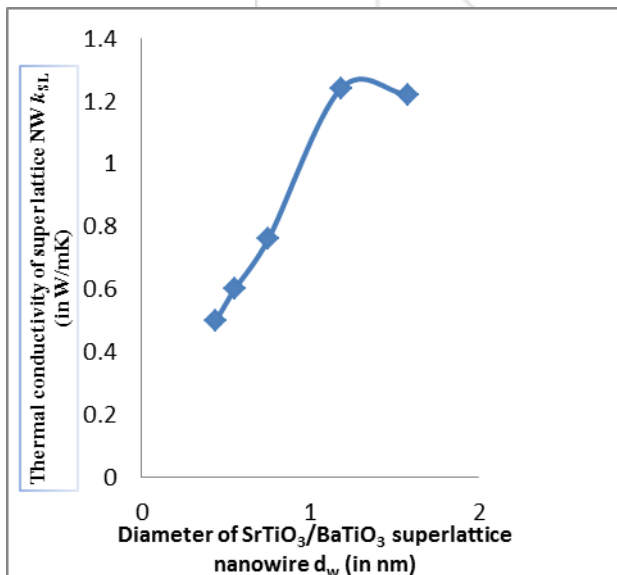
conductivity of individual nanodots ( $S$  and  $B$ ) is given by, [23]

$$\frac{L}{k_{SL}} = \frac{L_S}{k_{S,eff}} + \frac{L_B}{k_{B,eff}} \quad (8)$$

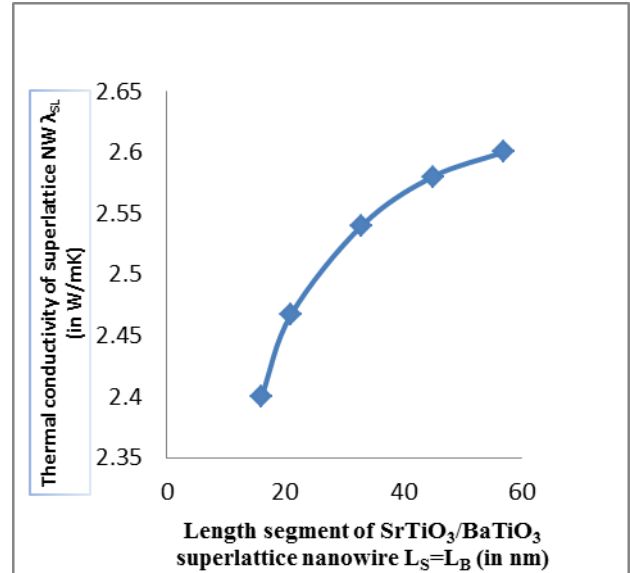
#### 4. Results and Discussion

The calculation of thermal conductivity of SrTiO<sub>3</sub>/BaTiO<sub>3</sub> superlattice nanowires can be done by keeping the length of the nanowire fixed at 300 K which is below the Debye temperatures of the bulk SrTiO<sub>3</sub> and BaTiO<sub>3</sub>. The periodic length for superlattice nanowires is  $L = L_{SrTiO_3} + L_{BaTiO_3} = 10$  nm having equal length segments, diameter of the nanowire is taken as 5 nm. The lattice thermal conductivity of SrTiO<sub>3</sub>/BaTiO<sub>3</sub> superlattice nanowire is calculated using the equation (8), the parameters of the bulk SrTiO<sub>3</sub> and bulk BaTiO<sub>3</sub> are taken through the references of previous research papers. The geometric factor  $\alpha$  is taken as 0.75. By varying length segments and diameters the values of lattice thermal conductivity of SrTiO<sub>3</sub>/BaTiO<sub>3</sub> superlattice nanowires can be find out and plot a graph to study its thermal characteristics.

The thermal conductivity of bulk BaTiO<sub>3</sub> is 2.65 W/mK [18] and mean free path of phonons is 2.3 nm [25] and the parameters for SrTiO<sub>3</sub> are its bulk thermal conductivity is 12 W/mK and mean free path of phonons is 2.35 nm. [14] By putting these parameters we can find the value of effective thermal conductivity of SrTiO<sub>3</sub> and BaTiO<sub>3</sub> and finally we study the variation in thermal conductivity by varying the diameters or length segments of superlattice nanowires by plotting graphs.



**Figure 2:** Relationship between diameter of nanowire and thermal conductivity of SrTiO<sub>3</sub>/BaTiO<sub>3</sub>.



**Figure 3:** Relationship between Length segment and thermal conductivity of SrTiO<sub>3</sub>/BaTiO<sub>3</sub>.

#### 5. Conclusions

The thermal conductivities of superlattice nanowire SrTiO<sub>3</sub>/BaTiO<sub>3</sub> samples were measured at room temperature, first by keeping the length segments constant having values of 5 nm and by varying the value of diameters as 0.44 nm, 0.55 nm, 0.75 nm, 1.18 nm and 1.58 nm and then by keeping the diameters constant and varying the value of length segments as 16 nm, 21 nm, 33 nm, 45 nm and 57 nm. The graph between the thermal conductivity and diameter of the superlattice nanowire keeping their length segments constant and the graph between thermal conductivity and length segment of superlattice nanowire keeping their diameters constant are plotted. The graphs show that as the total length of the superlattice nanowire is fixed, reducing the period length will lead to decreased effective thermal conductivity due to the increased number of interfaces. The reduced thermal conductivity of superlattice nanowire was found to be 0.5 W/mK for  $D_w = 0.44$  nm and  $L = 5$  nm, which is very much less than the thermal conductivities of bulk SrTiO<sub>3</sub> and bulk BaTiO<sub>3</sub> both at room temperature.

#### References

- [1] M. G. Kanatzidis et al., "New and Old Concepts in Thermoelectric Materials," *Angew. Chem. Int.*, (48), pp. 8616 – 8639, 2009.
- [2] J.-C. Zheng et al., "Recent advances on thermoelectric materials," *Front. Phys. China*, 3(3), pp. 269-279, 2008.
- [3] Masayuki Takashiri et al., "Cross-plane thermal conductivity of highly oriented nanocrystalline bismuth antimony telluride thin films," *Journal of Alloys and Compounds*, (490), pp. L44-47, 2010.
- [4] Joseph P. Heremans et al., "Resonant levels in bulk thermoelectric semiconductors," *Energy Environ. Sci.*, (5), pp. 5510–5530, 2012.
- [5] Bed Poudel et al., "High-Thermoelectric Performance of Nanostructured Bismuth Antimony Telluride Bulk Alloys," *Research Article, Science Express*, (320), pp. 634-638, 2008.

- [6] Yang, R. G., & Chen, G., "Nanostructured Thermoelectric Materials: From Superlattices to Nanocomposites," *Materials Integration*, 18(9), pp. 31-36, 2005.
- [7] Hiromichi Ohta et al., "High-temperature carrier transport and thermoelectric properties of heavily La- or Nb-doped SrTiO<sub>3</sub> single crystals," *Journal of Applied Phys.*, (97), pp. 034106, 2005.
- [8] Sean C. Andrews et al., "Atomic-level control of the thermoelectric properties in polytypoid nanowires," *Chem. Sci.*, (2), pp. 706–714, 2011.
- [9] Ming Hu et al., "Si/Ge Superlattice Nanowires with Ultralow Thermal Conductivity," *Nano Lett.*, (12), pp. 5487–5494, 2012.
- [10] Ali Shakouri et al., "Improved Thermoelectric Power Factor in Metal-Based Superlattices," *physical review letters*, (92), pp. 106103-106103, 2004.
- [11] Pankaj Jha et al., "Cross-plane electronic and thermal transport properties of p-type La<sub>0.67</sub>Sr<sub>0.33</sub>MnO<sub>3</sub>/LaMnO<sub>3</sub> perovskite oxide metal/semiconductor superlattices," *Journal Of Applied Physics*, (112), pp. 063714, 2012.
- [12] Shen, Yongxing, Annica Heyman, and Ningdong Huang. "Molecular Simulations of Thermal Conductivity of Si/SiGe Superlattice Nanowires," 2004.
- [13] Deyu Li et al., "Thermal conductivity of Si/SiGe superlattice nanowires," *Appl. Phys. Lett.*, (83), pp. 3186-3188, 2003.
- [14] G.H. Zheng et al., "Improvement of the Thermoelectric Properties of (Sr<sub>0.9</sub>La<sub>0.1</sub>)<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub> by Ag Addition," *J Low Temp Phys.*, (173), pp. 80–87, 2013.
- [15] Gautam G. Yadav et al., "Self-templated synthesis and thermal conductivity investigation for ultrathin perovskite oxide nanowires," *Nanoscale*, (3), pp. 4078-4081, 2011.
- [16] Jian Quan Qi et al., "Direct synthesis of ultrafine tetragonal BaTiO<sub>3</sub> nanoparticles at room temperature," *Nanoscale Research Letters*, (6), pp. 1-4, 2011.
- [17] Zhang, Rui-zhi, et al. "Thermoelectric transport coefficients of n-doped CaTiO<sub>3</sub>, SrTiO<sub>3</sub> and BaTiO<sub>3</sub>: A theoretical study." *Physica B: Condensed Matter*, (407), pp. 1114-1118, 2012.
- [18] Yi He et al., "Heat Capacity, Thermal Conductivity, and Thermal Expansion of Barium Titanate-Based Ceramics," *Thermochimica Acta*, (419), pp. 135–141, 2004.
- [19] N Papanikolaou et al., "Lattice thermal conductivity of SiC nanowires," *J. Phys.: Condens. Matter*, (20), pp. 6, 2008.
- [20] Yunfei Chen et al. "Monte Carlo Simulation of Silicon Nanowire Thermal Conductivity," *Journal of Heat Transfer*, (127), pp. 1129-1137, 2005.
- [21] Hopkins, Patrick E., et al., *ASME 2008 International Mechanical Engineering Congress and Exposition*. American Society of Mechanical Engineers, 2008.
- [22] K. A. Muller, Harry Thomas, "Structural Phase Transitions II," Springer Science & Business Media, (45), pp. 24, 2013.
- [23] Yu-Ming Lin et al., "Thermoelectric properties of superlattice nanowires," *Physical Review B*, (68), pp. 075304, 2003.
- [24] K. Keshoju et al., "Magnetic field driven nanowire rotation in suspension," *Appl. Phys. Lett.*, (91), pp. 123114, 2007.
- [25] Brian F. Donovan et al., "Supplementary Material: Spectral Phonon Scattering Effects on the Thermal Conductivity of Nano-Grained Barium Titanate," (105), pp. 082907, 2014.