

# The Properties of NbRhGe as High Temperature Thermoelectric Material

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**Abstract:** Energy deficit and the need for cleaner alternatives have necessitated the continued search for better energy generation technologies/materials. One of the advances of science and technology in this age is the capability to develop materials that can generate electricity when exposed to external stimulus such as a temperature gradient. Thermoelectric materials are material that can create electromotive force when exposed to temperature gradients. A new thermoelectric material, NbRhGe, have been studied using the density functional theory. The components of NbRhGe are not toxic neither can they suffer poor chemical and physical stability. The results showed that NbRhGe is a semiconductor with band-gap value of 1.62 eV. The compound is both elastically and thermodynamically stable, ductile and strong. It is a high temperature thermoelectric material with predicted figure of merit (ZT) value of 0.75 at 1050 K.

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## I. Introduction

The industrial growth and population increase has led to our over-utilization of natural resources, with its attendant impact on the environment and our lives. The need for more energy utilization is expected to increase, necessitating also, the need to look for alternative energy resources. This is not only to reduce the rate at which the present reserve is depleted, but to also obtain cleaner and safer alternatives. Energy loss in the form of heat is an integral part of almost all energy generation and consumption. The incident of global warming has stirred the need to cut down on fossil fuel powered plants, while alternative sources are sought in a sustainable manner. One of the advances of technology in this century is the ability to develop materials that can generate electrical energy in response to external stimuli, including temperature gradient, light, pressure etc.

The thermoelectric (TE) materials are group of materials that can convert heat to electrical energy under temperature gradients. The figure of merit (ZT),  $ZT = S^2\sigma T/\kappa$  ( $S$  = Seebeck coefficient;  $\sigma$  = electrical conductivity;  $\kappa$  = total thermal conductivity) is traditionally used to evaluate the efficiency of TE materials<sup>1</sup>. The ZT can be enhanced by doping or element addition/substitution. Many material compositions, including Bi<sub>2</sub>Te<sub>3</sub>, Sb<sub>2</sub>Te, SnSe, PbTe, PbS have experimentally shown to be efficient TE materials<sup>2,3,4</sup>. Apart from the fact that some of the constituent of these compounds are toxic, they suffer poor chemical and physical stability at high temperatures<sup>5,6</sup>. The semiconducting half-Heusler (HH) compounds have shown promise for TE applications<sup>7,8</sup>. Available data, had demonstrated large thermo-power, large Seebeck coefficients with moderate electrical conductivity in some semiconductor TE materials such as NiTiSn, TiCoSb and ZrCoSb<sup>9,10</sup>.

Thus, HH TE compounds are expected to receive more attention in times to come due to their robust mechanical cum thermal properties and environment friendly constituents. In pursuit of this, NbRhGe is proposed and investigated. Its composition is half Heusler, with properties such as the mechanical, electronic and transport properties investigated.

## II. Methodology

The ground state structure and the elastic parameters are obtained using the Quantum Espresso code<sup>11</sup>. The Perdew-Burke-Ernzerhof Generalized Gradient Approximation (GGA) is used to approximate the electron exchange-correlation functional<sup>12</sup>. The Monkhorst-Pack approach<sup>13</sup>, is used during integration on the irreducible Brillouin-zone. The optimized lattice parameter is calculated from a fit of the relaxed unit cell to a pressure-volume equation of state (EOS)<sup>14</sup>. The lattice dynamics due to phonons are calculated according to the framework of Density Functional Perturbation Theory<sup>11</sup>. The transport properties are calculated with the BoltzTraP code<sup>15</sup>. The code solves Boltzmann equations from which quantities that are band structure dependent are evaluated. Within constant time and the rigid band approximations<sup>16</sup>, the electrical conductivity ( $\sigma$ ), the Seebeck coefficient ( $S$ ) can be obtained using eq. 1 and eq. 2.

$$\sigma_{\alpha\beta}(\varepsilon) = \frac{e^2}{N} \sum_{i,k} \tau v_{\alpha}(i, k) \frac{\delta(\varepsilon - \varepsilon_{i,k})}{d\varepsilon}, \quad (1)$$

$$S_{ij} = E_i(\nabla_j T)^{-1} = (\sigma^{-1})_{\alpha_i} v_{\alpha_j}, \quad (2)$$

where  $\tau$ ,  $N$ ,  $\varepsilon$ ,  $\beta$ ,  $\alpha$  and  $v_{\alpha}(i, k)$  are the relaxation time, the number of sampled k-points, the band energy, tensor indices and the group velocity components respectively.

The group velocity can further be expressed as:

$$v_{\alpha}(i, k) = \frac{1}{\hbar} \frac{\partial \varepsilon_{i,k}}{\partial k_{\alpha}}, \quad (3)$$

Being function of chemical potential and temperature, the transport coefficients are calculated by integrating the transport distribution<sup>16</sup> such that:

$$v_{\alpha\beta}(T; \mu) = \frac{1}{eT\Omega\sigma_{\alpha\beta}(T, \mu)} \int \sigma_{\alpha\beta}(\varepsilon)(\varepsilon - \mu) \left[ -\frac{\partial f_{\mu}(T; \varepsilon)}{\partial \varepsilon} \right] d\varepsilon, \quad (4)$$

$$\kappa_{\alpha\beta}^0(T; \mu) = \frac{1}{e^2 T \Omega} \int \sigma_{\alpha\beta}(\varepsilon)(\varepsilon - \mu)^2 \left[ -\frac{\partial f_{\mu}(T; \varepsilon)}{\partial \varepsilon} \right] d\varepsilon, \quad (5)$$

where  $\Omega$  is the unit cell volume,  $\kappa^0$  is the electronic part of the thermal conductivity,  $e$  is the electronic charge,  $f_{\mu}$  is the Fermi–Dirac distribution function while  $\mu$ , is the chemical potential respectively.

### III. Results and Discussion

#### Electronic Properties

The crystal structure of NbGeRh is face centered cubic (space group = F-43m). The Wyckoff atomic positions are 4a (0, 0, 0) occupied by Nb, 4b (1/2, 1/2, 1/2) occupied by Ge and 4c (1/4, 1/4, 1/4) occupied by Rh respectively. The 4d site (3/4, 3/4, 3/4) is usually empty in the half-Heusler structure. The lattice constant, band gap and other calculated values on NbGeRh are given in Table no 1. The electronic structure of Nb, Rh and Ge are [4d<sup>4</sup> 5s<sup>1</sup>], [4d<sup>8</sup> 5s<sup>1</sup>] and [4s<sup>2</sup> 4p<sup>2</sup>] respectively. The Pauling-Slater equation [ $M_t = (Z_t - 18)\mu_B$ ] provides easy way to check if a half-Heusler thermoelectric material is a metal or semiconductor and also whether it is magnetic or non-magnetic<sup>17</sup>.

**Table no 1:** Calculated bulk modulus, lattice constant, band gap and the pressure derivative of NbGeRh.

Properties	Result
Lattice constant ( $\text{\AA}$ )	5.969
Bulk modulus $B_0$ (GPa)	175.30
Pressure derivative of $B'$ (GPa)	4.59
Band gap, $E_g$ (eV)	1.627

Using the Pauling-Slater relation, the hybridization of the orbitals of NbRhGe points to a non-magnetic semiconducting material because the magnetic moment ( $M_t$ ) will be  $0.0\mu_B$  since  $Z_t$  (the total sum of all valence electrons) gives 18. The calculation of the density of states (DOS) or the energy bands along high symmetry paths becomes useful when one needs to understand material types (i.e. metal, semiconductor or insulator). The two plots are given in Fig. 1. Fig. 1(a) (band structure result) reveals that the maximum valence band energy (which occurs at the  $\mathbf{L}$  symmetry point) is at different momentum compared with the minimum conduction band energy which is at the  $\mathbf{X}$  symmetry point. This, thus show that NbGeRh is a semiconductor with an indirect band gap. The size of the band gap is 1.627 eV. The possession of gap at E-E<sub>F</sub> of the DOS (Figure 1b) confirms further that NbGeRh is semiconductor in nature. It can be seen near E-E<sub>F</sub>, that majority of the DOS is due to hybridization of Nb and Rh d-states.

#### Mechanical Properties

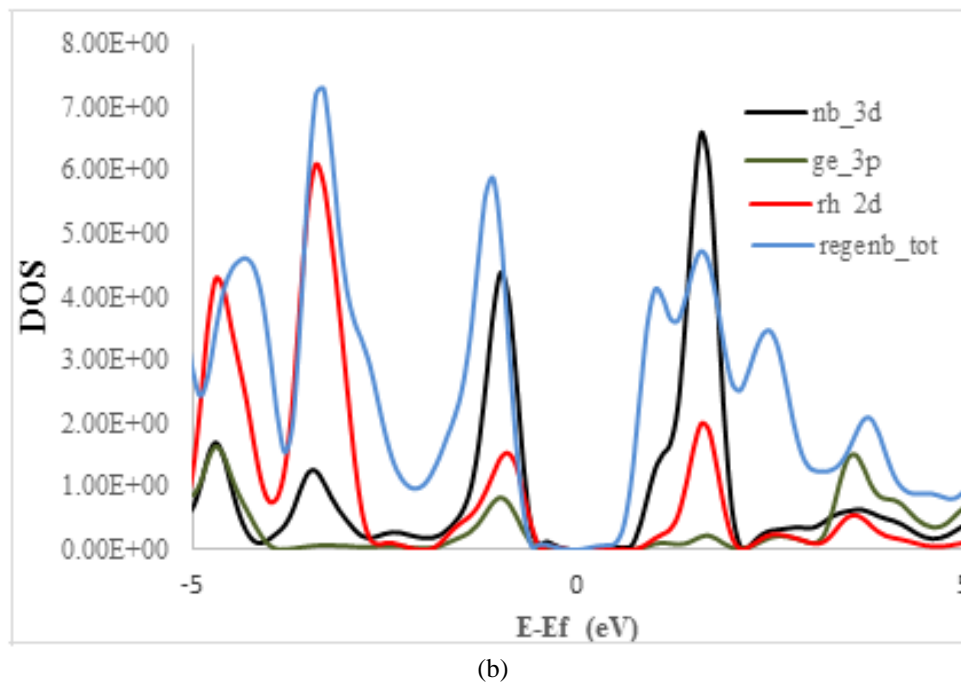
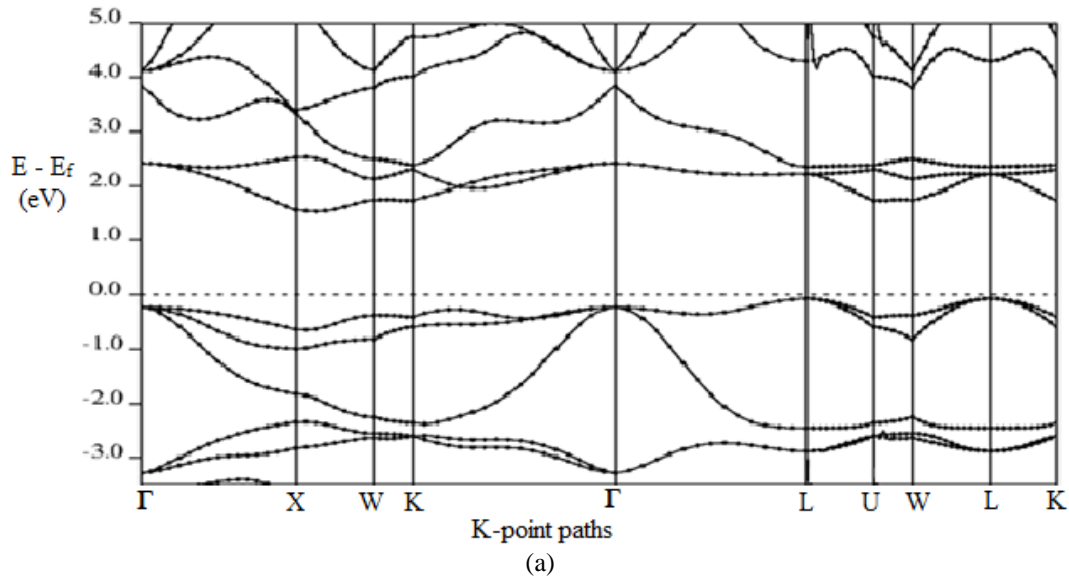
The calculated mechanical properties include the elastic constants, bulk modulus ( $B$ ) and the shear modulus ( $G$ ). The results are listed in Table no 2. A material's stiffness against strains can be gauged with  $c_{11}$  while  $c_{44}$  can be used to evaluate a material's resistance towards shear deformation. A cubic lattice is mechanically stable<sup>18</sup>, when it satisfies the stability criteria in eq. 6.

$$c_{11}-c_{12} > 0, c_{11} > 0, c_{44} > 0 \text{ and } (c_{11}+2c_{12}) > 0 \quad (6)$$

The elastic constants in Table no 2, satisfy the stability criteria and therefore, NbGeRh is mechanically stable. The shear ( $G$ ) and bulk ( $B$ ) moduli have been estimated using the Hill approximation<sup>19</sup>. The value of  $B$  obtained with this approximation (183.34 GPa) deviate a little from the value of  $B$  obtained by the EOS (175.30 GPa). This confirms that the structure was adequately optimized and therefore the good self-consistency of the calculation. The other two mechanical properties calculated are the Poisson's ratio ( $\nu$ ) and the Young's modulus ( $Y$ ). They have been calculated using:

$$\nu = \frac{(3B-2G)}{2(3B+G)} \quad (7)$$

$$Y = \frac{9BG}{3B+G} \quad (8)$$



**Fig. 1** (a) Energy bands along high symmetry paths and (b) density of states of NbRhGe.

The Pugh ratio helps to estimate brittleness or ductility in a material. A material is ductile if its Pugh ratio ( $B/G$ ) is  $> 1.75$ , otherwise it will be brittle<sup>20</sup>. The Pugh ratio for NbGeRh is 2.97, meaning that the compound will be ductile in nature. The Frantsevich's ratio is given as  $G/B$ . Any material with Frantsevich ratio

less than 1.06 would be ductile. The calculated  $G/B$  for NbGeRh is 0.37, indicating further that the compound is ductile. Hardness is an important property for structural materials. There are several scales on which it is measured. The Vicker's scale<sup>21</sup> can predict hardness using eq. 9.

$$H_v = 0.92(B/G)^{1.3137}G^{0.708} \quad (9)$$

Any material with  $H_v > 40$  GPa are classified as super-hard material<sup>22</sup>. With a calculated value of  $H_v = 71.17$  GPa, NbGeRh can be considered to be a super-hard material. Anisotropy in a material can be gauged from the elastic constants. There are three indexes that can be used - a universal ( $A^U$ ) index, a compression ( $A_B$ ) index and the shear ( $A_G$ ) index respectively. The calculation formulas<sup>23,24</sup>, are expressed in eq. 10 – eq. 12.

$$A^U = 5 \frac{G_V}{G_R} + \frac{B_V}{B_R} - 6, \quad (10)$$

$$A_B = \frac{B_V - B_R}{B_V + B_R}, \quad (11)$$

$$A_G = \frac{G_V - G_R}{G_V + G_R}, \quad (12)$$

**Table no 2:** Calculated elastic constants ( $c_{11}, c_{12}, c_{44}$ ), bulk modulus ( $B$ ), shear modulus ( $G$ ), Young modulus ( $Y$ ), Poisson's Ratio ( $\nu$ ), Pugh Ratio ( $B/G$ ), Frantsevich's Ratio ( $G/B$ ) and Vickers Hardness ( $H_v$ ) on NbGeRh.

Properties	Calculated values	Properties	Calculated values
$c_{11}$ (GPa)	243.91	$G$ (GPa)	61.68
$c_{12}$ (GPa)	153.06	$Y$ (GPa)	166.38
$c_{44}$ (GPa)	75.71	Poisson's Ratio ( $\nu$ )	0.35
$c_{11} - c_{12}$ (GPa)	90.85	Pugh Ratio ( $B/G$ )	2.97
$c_{11} + 2c_{12}$ (GPa)	550.03	Frantsevich's Ratio ( $G/B$ )	0.37
$B$ (GPa)	183.34	Vickers Hardness ( $H_v$ )	71.17

A value of zero for any of the indexes depicts isotropy while variation from zero stands for an anisotropic material. The calculated  $A^U$  value for NbGeRh is 0.320 (see Table no 3), indicating it would exhibit anisotropic behavior. While NbGeRh will exhibit isotropic compression (because  $A_B = 0.000$ ), it is predicted to exhibit shear anisotropy (due to  $A_G = 0.031$ ). The bond between atoms in crystal planes can have varying degree of anisotropy<sup>25</sup>. This can be evaluated using the shear anisotropic factors  $A_1$  in eq. 13 for the {100} plane,  $A_2$  in eq. 14 for the {010} plane and  $A_3$  in eq. 15 for the {001} plane.

$$A_1 = \frac{4c_{44}}{c_{22} + c_{33} - 2c_{13}} \quad (13)$$

$$A_2 = \frac{2c_{44}}{c_{11} - c_{12}} \quad (14)$$

$$A_3 = \frac{2c_{44}}{c_{11} - c_{12}} \quad (15)$$

A material is considered to be isotropic along the plane in which its shear anisotropic factor is 1. Any deviation from 1 means the material is anisotropic along the plane. From the results in Table no 3,  $A_1 = A_2 = A_3 = 1.667$ , indicating that NbGeRh crystal would exhibit shear anisotropy in all the three planes.

**Table no 3:** The calculated universal ( $A^U$ ), compression ( $A_B$ ), shear ( $A_G$ ) and planar ( $A_1, A_2, A_3$ ) anisotropy indexes for NbGeRh.

l Anisotropic index	$A^U$	$A_B$	$A_G$	$A_1$	$A_2$	$A_3$
Value	0.32	0.00	0.031	1.667	1.667	1.667

### Phonon Properties

There are three atoms in the primitive cell of NbGeRh. The three atoms ( $N$ ) are expected to give rise to  $3N$  ( $3 \times 3 = 9$ ) phonon branches (three acoustics and six optical modes) as seen in Fig. 2<sup>26</sup>. The acoustic modes begin at  $\Gamma$ -point and increases with frequency in a linear fashion. While the optical branch contributes little to lattice vibrations, the acoustic mode is responsible for maximum heat transfer due to its large group velocities that almost reach  $200 \text{ cm}^{-1}$ . A considerable mixing (good for thermoelectric application) between the acoustic and optical branches is lacking in Fig. 2. Based on Fig. 2, it can be predicted that NbGeRh is structurally and thermodynamically stable due to the sole existence of its phonon dispersion in the positive frequency domain.

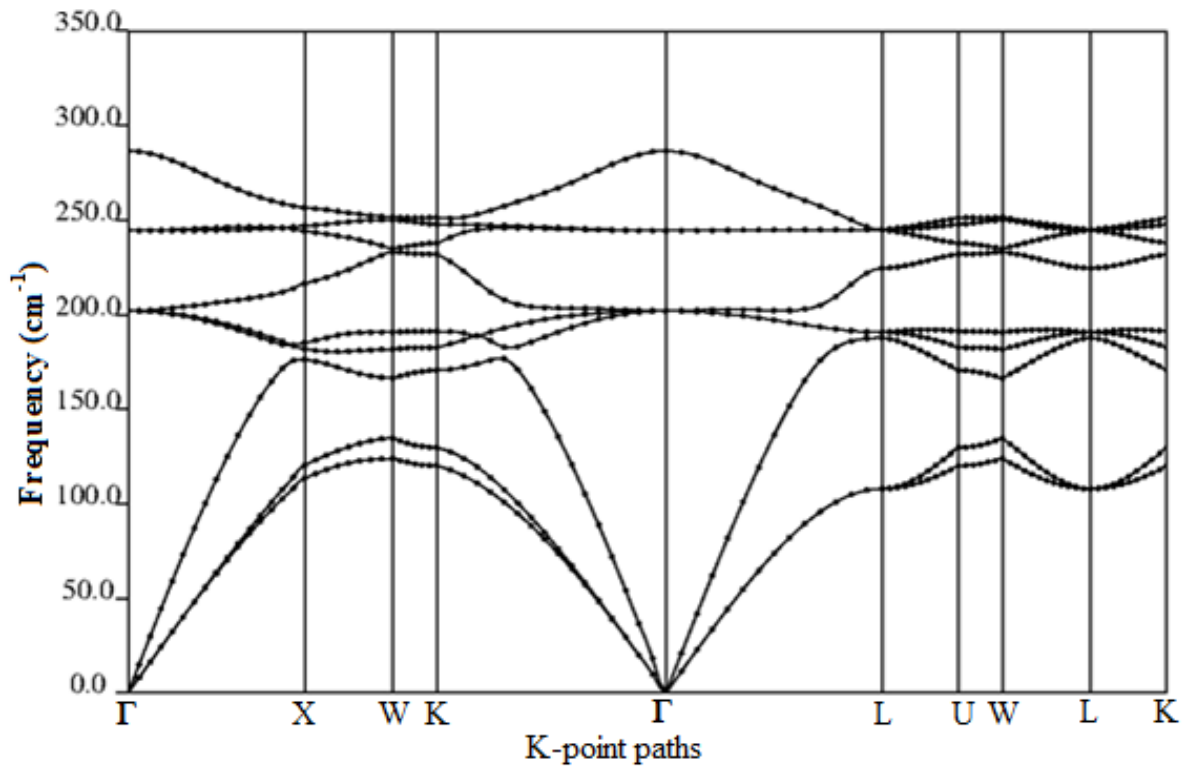
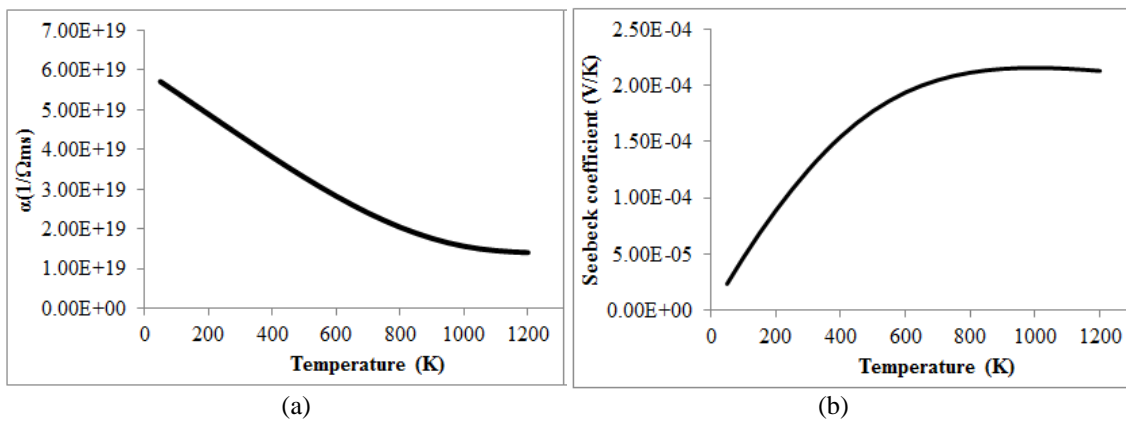


Fig. 2 Phonon dispersion for NbGeRh

**Thermoelectric Properties**

The variation of the Seebeck coefficient with temperature for NbRhGe around the Fermi level is depicted in Fig. 3(a). The Seebeck coefficient is positive within optimal carrier concentration, thereby predicting NbRhGe to be a p-type semiconductor. It is noted that the calculated Seebeck coefficient ( $S$ ) increases with temperature from about  $125\mu\text{V/K}$  at room temperature and attains peak value at about 1050 K. The variation of electrical conductivity ( $\sigma$ ) with temperature is shown in Figure 3(b). It is clear from this figure that the electrical conductivity ( $\sigma$ ) has a decreasing trend with temperature. This isn't surprising as the Seebeck coefficient is a function of carrier concentration and mobility. Also, mobility is inversely related to temperature. Therefore, any temperature increase would increase carrier concentration but reduce mobility and hence electrical conductivity as seen in Fig. 3(b). The effect of temperature on the electronic thermal conductivity is shown in Fig. 3(c). As temperature increases so is the electronic thermal conductivity in NbRhGe. The ZT result, calculated from  $S$ ,  $\sigma$  and  $\kappa$  is presented in Fig. 3(d). A ZT value of 0.75 is predicted for NbRhGe at 1000 K.



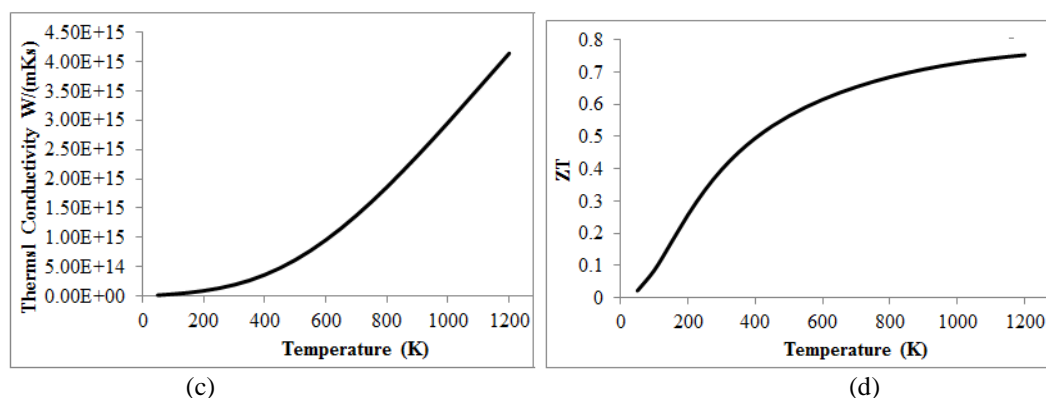


Fig. 3 Thermoelectric parameters: (a) Seebeck coefficient (b) Electrical conductivity (c) Thermal conductivity and (d) Figure of merit

#### IV. Conclusion

A number of *ab initio* tools have been used to investigate the electronic, mechanical and the thermoelectric properties of NbGeRh. The elastic constants and the phonon dispersion predict NbGeRh to be mechanically and thermodynamically stable. It is an indirect band gap semiconductor. The elastic and thermoelectric properties, particularly the Seebeck coefficient, the electrical conductivity and the electronic thermal conductivity trends are normal. Further investigation of the material, particularly its lattice thermal conductivity is suggested. Putting in perspective the optimum mechanical properties of NbGeRh, it is believed the material could serve as the basis for experimentalist in the design of high temperature thermoelectric material.

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