

Article

High-Throughput Screening of High-Performance Thermoelectric Materials with Gibbs Free Energy and Electronegativity

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Abstract: Thermoelectric (TE) materials are an important class of energy materials that can directly convert thermal energy into electrical energy. Screening high-performance thermoelectric materials and improving their TE properties are important goals of TE materials research. Based on the objective relationship among the molar Gibbs free energy (G_m), the chemical potential, the Fermi level, the electronegativity (X) and the TE property of a material, a new method for screening TE materials with high throughput is proposed. This method requires no experiments and no first principle or Ab initio calculation. It only needs to find or calculate the molar Gibbs free energy and electronegativity of the material. Here, by calculating a variety of typical and atypical TE materials, it is found that the molar Gibbs free energy of Bi_2Te_3 and Sb_2Te_3 from 298 to 600 K ($G_m = -130.20 \sim -248.82$ kJ/mol) and the electronegativity of Bi_2Te_3 and Sb_2Te_3 and PbTe ($X = 1.80 \sim 2.21$) can be used as criteria to judge the potential of materials to become high-performance TE materials. For good TE compounds, G_m and X are required to meet the corresponding standards at the same time. By taking $G_m = -130.20 \sim -248.82$ kJ/mol and $X = 1.80 \sim 2.21$ as screening criteria for high performance TE materials, it is found that the G_m and X of all 15 typical TE materials and 9 widely studied TE materials meet the requirement very well, except for the X of Mg_2Si , and 64 pure substances are screened as potential TE materials from 102 atypical TE materials. In addition, with reference to their electronegativity, 44 pure substances are selected directly from a thermochemical data book as potential high-performance TE materials. A particular finding is that several carbides, such as Be_2C , CaC_2 , BaC_2 , SmC_2 , TaC and NbC , may have certain TE properties. Because the G_m and X of pure substances can be easily found in thermochemical data books and calculated using the X of pure elements, respectively, the G_m and X of materials can be used as good high-throughput screening criteria for predicting TE properties.

Keywords: high-throughput screening; thermoelectric materials; Gibbs free energy; electronegativity; screening criteria for thermoelectric materials



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1. Introduction

Thermoelectric (TE) materials have received widespread attention around the world due to their ability to convert heat and electricity directly to each other. Improving their thermoelectric conversion efficiency or finding materials with high thermoelectric properties is a very important goal of thermoelectric material research. In principle, the thermoelectric figure of merit $Z = \alpha^2 \sigma / K$ or $ZT = \alpha^2 \sigma T / K$ (α , σ , K and T are the Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature of the material, respectively) is not only a parameter used to evaluate the performance of a TE material but also a theoretical basis for exploring high-performance TE materials. However, since the ZT of thermoelectric materials usually varies significantly with carrier concentration

and temperature, thermoelectric materials with an unknown optimum doping concentration and the maximum figure of merit can only be evaluated by preparing numerous samples with different doping concentrations to measure and analyze the parameters over a wide temperature range. Obviously, the time from material composition design, weighing, synthesis and sintering to thermoelectric property testing and a performance analysis will take as little as three months or as much as one year. Therefore, it is difficult to use Z or ZT values to quickly analyze and judge a large number of unknown materials one by one. With the implementation of genetic engineering projects in recent years, the screening of thermoelectric materials using high-throughput calculations has received widespread attention worldwide. The mainstream high-throughput screening methods are theoretical calculations based on density functional theory and the Boltzmann equation, which establishes the relationship between the lattice structure and the thermoelectric transport coefficient of a material, and uses descriptors such as low thermal conductivity, thermoelectric superiority or the power factor to characterize the thermoelectric properties of the material. For example, elastic properties are used to efficiently evaluate the intensity of anharmonicity and lattice thermal conductivity for the high-throughput and efficient screening of thermoelectric materials with low lattice thermal conductivity [1]. But the high-throughput calculations and screening of high-performance thermoelectric materials also face two important difficulties: (1) precise calculations of the electrical and thermal properties of the materials are difficult and time-consuming, and (2) the existing high-throughput methods for evaluating the electrical and thermal properties of the materials have limitations.

Therefore, there is an urgent need for a simple and effective method to make a preliminary determination of the level of thermoelectric properties of a material or a criterion to determine its potential to become a high-performance thermoelectric material. Earlier, based on the thermoelectric figure of merit (Z) proportional to the previously derived material parameter β (see Equations (1) and (2)), Ioffe proposed a method for finding high-performance TE materials using the β value [2].

$$ZT = \frac{[\xi - (s + \frac{5}{2})]^2}{(\beta \exp \xi)^{-1} + (s + \frac{5}{2})} \quad (1)$$

$$\beta = 5.745 \times 10^{-6} \frac{\mu_c}{K_L} \left(\frac{m^*}{m} \right)^{3/2} T^{5/2} \quad (2)$$

where ξ , s , μ_c , K_L , m^* , and m are the reduced Fermi level, scattering factor, carrier mobility, lattice thermal conductivity, effective mass, and the mass of the free electron, respectively. In Formula (2), the effective mass m^* , lattice thermal conductivity K_L and carrier mobility μ_c are generally weakly dependent on the carrier concentration, so the β parameter can be used to initially determine the thermoelectric properties of a material, even for samples that are not optimally doped. Accordingly, Ioffe believes that an effective way to find thermoelectric materials is to first screen the materials for lattice thermal conductivity and then make a further determination by measuring the $(m^*)^{3/2} \mu_c$ value of the materials. It is clear that this method avoids the requirement of the optimal doping of the sample, and it is much simpler than the method that uses the original formula of the thermoelectric figure of merit Z or ZT . Nevertheless, the determination of the β parameter involves the measurement of carrier mobility (μ_c) and effective mass (m^*), both of which are more complex to measure than the Seebeck coefficient (α) and electrical conductivity (σ), thus limiting the practical application of this approach. It is also essential to note that, while the variation in the β parameter with carrier concentration is much less pronounced than the thermoelectric figure of merit, it is not a constant.

Based on many years of practice, a number of useful laws, for example, heavy atomic mass [3], a large Fermi surface complexity factor [4], multiple energy valley degeneracies [5,6] or a complex Fermi surface structure [7], the appropriate carrier concentration [8],

resonance energy levels [9,10], the energy-filtering effect [11], strong phonon scattering [12], strong anharmonic effects [13] and Phonon Glass–Electron Crystal (PGEC) properties [14], have been gradually obtained that summarize the physical properties of a good thermoelectric material. Among them, the use of materials with a high average relative atomic mass to improve m^*/K_L and, thus, thermoelectric properties as criteria for selecting thermoelectric materials was first proposed by Goldsmid [15]. This rule was supplemented in 1995 by Slack et al., who noted the relationship of the electronegativity (X) of compounds with mobility, the effective mass and the forbidden band width, and they proposed the use of the electronegativity of compounds as a metric for the first screening of thermoelectric materials. This law can be briefly stated as follows: (1) The greater the sum of the atomic numbers of a compound, the larger the cell size, and the lower the thermal conductivity in general. (2) The smaller the electronegativity of a compound, the larger the product of the effective mass and mobility generally [16]. While the laws summarized by Goldsmid and Slack are useful for a preliminary judgment of element choices for thermoelectric materials, they do not provide sufficient insight into the effects of the elements in the periodic table on the thermoelectric properties of materials. The other parameters listed above suffer from similar problems as β . They all require extensive experimental measurements or calculations to be obtained. They cannot be used as simple, fast and effective criteria to judge whether a compound or alloy has a high thermoelectric performance or thermoelectric figure of merit.

Obviously, the ideal way to find promising thermoelectric materials in a wide variety of materials is to make preliminary judgments based on the periodic table of the elements and the known basic physical properties of the elements. Moreover, it is a fact that there is a wealth of molar Gibbs free energy (G_m) data or thermochemical data of pure substances and convenient calculation methods for molar Gibbs free energy. In this paper, firstly, the rationality of using molar Gibbs free energy to evaluate the thermoelectric properties of materials is described. Then, the molar Gibbs free energy of a series of typical and atypical pure compound thermoelectric semiconductor materials is shown, the electronegativity (X) of the corresponding materials is calculated, and the change rule is analyzed. A new method using the molar Gibbs free energy and electronegativity of pure compounds as a fast and high-throughput preliminary screening method for thermoelectric materials is discussed.

2. Basal Principle

2.1. Fermi Level as a Criterion for High-Performance Thermoelectric Materials

This paper assumes that there is only one type of carrier that obeys the Fermi–Dirac statistical distribution, the isoenergy surface is spherical, the energy band is parabolic, the relaxation time approximation can be used to describe the scattering process in the crystal, and the contribution of the drag effect can be neglected; furthermore, the Fermi level E_F is considered an independent variable. The relationship between the reduced Fermi level ξ ($\xi = E_F/k_B T$), the Seebeck coefficient (α) and the conductivity (σ) of a material under different degenerate conditions can be seen in Table 1.

Table 1. The Seebeck coefficients and electrical conductivities under different ξ values.

ξ	Seebeck Coefficient (α)	Electrical Conductivity (σ)
Any ξ	$\alpha_{p,n} = \pm \frac{k_B}{e} \left(\frac{(s+\frac{5}{2})F_{s+\frac{3}{2}}(\xi)}{(s+\frac{3}{2})F_{s+\frac{1}{2}}(\xi)} - \xi \right)$	$\sigma = \frac{16\pi e^2 \tau_0 (2m^*)^{1/2} (k_B T)^{3/2+s}}{3h^3} (s+\frac{3}{2})F_{s+1/2}(\xi)$
$\xi \ll 1$	$\alpha = \pm \frac{k_B}{e} [(s+\frac{5}{2}) - \xi]$	$\sigma = \frac{16\pi e^2 \tau_0 (2m^*)^{1/2} (k_B T)^{3/2+s}}{3h^3} \Gamma(s+\frac{5}{2}) \exp(\xi)$
$\xi > 4$	$\alpha = \pm \frac{\pi^2 k_B}{3e} \frac{(s+\frac{3}{2})}{\xi}$	$\sigma = \frac{16\pi e^2 \tau_0 (2m^*)^{1/2}}{3h^3} E_F^{s+3/2}$

As mentioned above, in order to obtain a high thermoelectric figure of merit, Ioffe proposed [15] the use of the β factor to predict the thermoelectric performance of a material. It is believed that the greater the β value, the higher the thermoelectric performance of the material. On this basis, in 1959, Chasmar and Stratton used the Fermi–Dirac statistic to rigorously calculate the dependence of the dimensionless value $ZT_{\max}$ on the reduced Fermi level ξ ($\xi = E_F/k_B T$), the β factor and the scattering factor (s). The results are shown in Table 2 [17,18].

Table 2. Correspondence amongst the optimal reduced Fermi level (ξ_{opt}), the scattering factor (s), the material parameter (β) and the figure of merit ($ZT_{\max}$).

S	β	0.1	0.2	0.5	1.0	2.0	5.0
−1/2	$ZT_{\max}$	0.4	0.6	1	1.8	2.9	4.6
	ξ_{opt}	−0.1	−0.1	−0.8	−1.0	−1.7	−2.4
1/2	$ZT_{\max}$	0.8	1.1	2.0	2.8	3.8	5.6
	ξ_{opt}	0.8	0.35	−0.4	−0.9	−1.6	−2.3
3/2	$ZT_{\max}$	1.4	2.0	2.8	3.8	5.0	6.6
	ξ_{opt}	1.2	0.5	−0.3	−0.8	−1.5	−2.2

It can be found that the $ZT_{\max}$ value increases with an increase in the scattering factor (s) and the β value, but it increases with a decreasing optimal reduced Fermi level (ξ_{opt}). In addition, in correspondence to the different scattering mechanisms, the optimal reduced Fermi level (ξ_{opt}) also has a certain range of variation. When $s = -1/2$ and $1 \leq \beta \leq 5$, the $ZT_{\max}$ is between 1.8 and 4.6, and the ξ_{opt} is between −1.0 and −2.4. An inverse relationship can also be seen between $ZT_{\max}$ and ξ_{opt} .

Furthermore, in 1972, Ure [18,19] used a two-band model and disregarded the effects of multi-valley and non-spherical isoenergetic surfaces to avoid excessive complexity. In the study, Ure considered the effects of lattice thermal conductivity and bipolar diffusion and adopted the elastic constant ($1.7 \times 10^{11} \text{ Nm}^{-2}$), the deformation potential constant D (7 eV) and the effective mass m^* (0.014 m) of silicon. For the case where acoustic phonon scattering predominates, Ure used this method to estimate the actual optimal values of thermoelectric materials. The results indicated that the dimensionless optimal upper limit was $ZT_{\max} \approx 8$, corresponding to the optimal reduced Fermi level $\xi_{\text{opt}} \approx -3.0$.

As explained in the previous paragraph, it should be emphasized that, although the formulas in Table 1 are based on the above assumptions, the conclusion that the Fermi level and the scattering factor have a decisive effect on the thermoelectric properties of a material is universal. Based on the research results of the related literature on the effects of two kinds of carriers (including holes and electrons), an asymmetric band structure and a dual-band structure (considering a conduction band and a valence band) on thermoelectric properties, it can be confirmed that the Fermi level and scattering factor have a decisive influence on the thermoelectric properties of materials [20–23]. In addition, the typical high-performance thermoelectric materials known to us, such as bismuth telluride, antimony telluride and lead telluride, have more energy valleys. Therefore, the conclusion that Fermi levels and scattering factors have a decisive effect on the thermoelectric properties of materials is universal.

Summarizing the research results reported above, it should be possible to give a preliminary judgment on the thermoelectric performance of a material based on the Fermi level (E_F) or reduced Fermi level (ξ). Therefore, the relationship between the Gibbs free energy and the Fermi level (E_F) of materials is discussed.

2.2. The Relationship between Molar Gibbs Free Energy and Fermi Level

According to thermodynamics theory, the Gibbs free energy $G(T, P, N)$ of a material system has an extensive property, where T , P and N are the absolute temperature, pressure and moles of a pure substance. The $G(T, P, N)$ of the system is equal to the product of the number of moles of the substance (N), and the molar Gibbs free energy $G_m(T, P)$ is equal to the chemical potential (μ) of that substance. This can be expressed as [24,25]

$$\mu = G_m(T, P) = \frac{G(T, P, N)}{N} = H - TS \quad (3)$$

where $G_m(T, P)$ (G_m for short), H and S are the Gibbs free energy, enthalpy and entropy per mole of a pure substance.

At 0 K, the Fermi level (E_F) of a pure substance is equal to its chemical potential μ [24], namely,

$$E_F = \mu \quad (4)$$

By substituting Formula (3) into Formula (4), we can obtain the following formula:

$$E_F = \mu = G_m(T, P) = H - TS \quad (5)$$

In Formula (5), it appears that the Fermi level can be solved using the molar Gibbs free energy of the material. However, in addition to the fact that the two are equal at absolute temperatures and not necessarily exactly equal at other temperatures, the ground states calculated for the two are also different. E_F has a ground state temperature of 0 K. That is, the Fermi energy is defined as the energy of the topmost filled level in the ground state of the N electron system. The ground state is the state of the N electron system at absolute zero. However, by definition, for a homogeneous crystal with a uniform temperature, S is calculated as [26]

$$S(T) = k \ln \Omega_C(T = 0) + \int_0^T (C_p/T) dT \quad (6)$$

where $C_p(T)$ and Ω_C are the isobaric heat capacity and the thermodynamic probability of the material, respectively. For a perfect crystal, $\Omega_C(T = 0) = 1$; that is, $S(T = 0) = 0$.

The enthalpy $H(T, P)$ (H for short) of a pure substance is described entirely by independent internal variables T and P . The state function $H(T, P)$ is determined when the pressure P is constant, except for additional uncertain and arbitrarily selected constants. In other words, for any system, the absolute value of enthalpy (H) cannot be determine. For this reason, different books use different conventions for the zero of H , such as the data cited here stating that the standard enthalpy H of all pure elements in its reference phase is zero at $P = 1$ bar and $T = 298.15$ K. Therefore, when using enthalpy values from different sources, we must pay attention to the standard state of the reference phase. For pure material enthalpy, its calculation formula can be expressed as [26]

$$H(T) = H(298.15) + \int_0^{T_{t1}} C_p(T) dT + \Delta H_{t1} + \int_{T_{t1}}^{T_{t2}} C_p(T) dT + \Delta H_{t2} + \dots \quad (7)$$

where $H(298.15)$ is the enthalpy of the formation of pure matter at 1 bar and 298.15 K, $C_p(T)$ is the temperature function of the heat capacity, and ΔH_{t1} is the enthalpy of the phase transition at temperature $T = T_{t1}$. The corresponding entropy calculation Formula (6) can also be expressed as follows:

$$S(T) = S(298.15) + \int_0^{T_{t1}} \frac{C_p(T)}{T} dT + \frac{\Delta H_{t1}}{T_{t1}} + \int_{T_{t1}}^{T_{t2}} \frac{C_p(T)}{T} dT + \frac{\Delta H_{t2}}{T_{t2}} + \dots \quad (8)$$

$$S(298.15) = S(T = 0) + \int_0^{298.15} dH/T \quad (9)$$

$$S = k \ln \Omega_C(T = 0) + \int_0^T (C_p/T) dT \quad (10)$$

For a complete crystal, at $T = 0$ K, $S = 0$, which is $\Omega = 1$.

$$S(298.15) = \int_0^{298.15} dH/T \quad (11)$$

Then, the molar Gibbs free energy of a pure substance at 1 bar can be calculated as follows:

$$G_m(T) = G_m(298.15) + \int_0^{T_{t1}} C_p(T) dT + \Delta H_{t1} + \int_{T_{t1}}^{T_{t2}} C_p(T) dT + \Delta H_{t2} - T \left(\int_0^{T_{t1}} \frac{C_p(T)}{T} dT + \frac{\Delta H_{t1}}{T_{t1}} + \int_{T_{t1}}^{T_{t2}} \frac{C_p(T)}{T} dT + \frac{\Delta H_{t2}}{T_{t2}} + \dots \right) \quad (12)$$

$$G_m(298.15) = H(298.15) - TS(298.15) \quad (13)$$

In Equation (13), $H(298.15)$ and $S(298.15)$ are the standard enthalpy and the standard entropy of the pure substance, respectively. Therefore, $G(T)$ function values are also involved in the $H(T)$ convention. Thus, the molar Gibbs free energy of the reference phase of an element E at 198.15 K and 1 bar is given by using the following formula:

$$G_m(298.15) = -TS(298.15) \quad (14)$$

If there is no phase transition, Equation (12) can be simplified as follows:

$$G_m(T) = G_m(298.15) + \int_0^T C_p(T) dT - T \int_0^T \frac{C_p(T)}{T} dT \quad (15)$$

Therefore, the chemical potential (μ) or Fermi level (E_F) cannot be calculated simply from the data of the molar Gibbs free energy. However, because of the inevitable relationship between the two, we can still summarize the inevitable relationship between the change law of the molar Gibbs free energy data of thermoelectric materials and the thermoelectric properties of materials and use it as one of the methods for the high-throughput screening of thermoelectric materials.

In addition, as mentioned above, Slack et al. noted the relationship between the electronegativity and mobility, effective mass and band gap width in compounds, and they proposed using the electronegativity of a compound as a metric for a preliminary screening of thermoelectric materials [16]. To this end, following the example of Bulter and Ginley et al., the electronegativity X of the semiconductor compound A_nB_m is calculated using the geometric mean value of Mulliken electronegativity [27,28]:

$$X = (\chi_A^n \chi_B^m)^{1/(n+m)} \quad (16)$$

where χ_A and χ_B are the electronegativity of pure elements A and B, respectively.

3. Results and Discussion

Except for special emphasis, the molar Gibbs free energy (G_m) data are selected from Ihsan Barin's *Thermochemical Data of Pure Substances* [26] or the *Handbook of Inorganic Thermodynamics Data* [29].

3.1. Molar Gibbs Free Energy (G_m) of Pure Elements Listed in the Seebeck and Meissner Sequences

The G_m s of the substances listed in the Seebeck and Meissner sequences [30] are shown in Table 3. The elements with high Seebeck coefficients listed in both sequences are Bi and Sb. Their G_m values are between -13.572 and -38.325 kJ/mol. Moreover, it is found that their G_m values decrease with an increase in the temperature (the absolute value increases). If $G_m = -13.572$ and

−38.325 kJ/mol are taken as screening criteria, all elements in Table 3, except for element C, may have certain TE properties in the appropriate temperature range, of which the difference is that their optimal working temperature zones are different. At room temperature, only the G_m values of Na, U, Sn, Cd and Au meet the requirements. Although the G_m values of K, Hg, Pb and Cs at 298.15 K are within the above range, their absolute G_m values are larger or comparable to the G_m values of Bi or Sb at higher temperatures, so it is judged that these four elements may have better thermoelectric properties at slightly higher temperatures.

Table 3. Temperature dependence of the G_m of elementary substances listed in Seebeck and Meissner sequences.

Seebeck Sequence	Meissner Sequence	$\alpha/(\mu\text{V/K})$	$G_m/\text{kJ/mol}$								
			298 K	300 K	400 K	500 K	600 K	700 K	800 K	900 K	1000 K
Bi	Bi	−70	−16.916	−17.021	−23.098	−29.848	−38.325	−48.221	−58.528	−69.185	−80.151
Co	Co	−17.5	−8.957	−9.012	−12.414	−16.483	−21.119	−26.25	−31.888	−37.932	−44.361
Ni	Ni	−18	−8.907	−8.962	−12.371	−16.496	−21.243	−26.557	−32.322	−38.478	−44.99
	K	−12	−19.281	−19.401	−26.798	−35.244	−44.309	−53.879	−63.876	−74.247	−84.952
Pd	Pd	−6	−11.277	−11.347	−15.541	−20.408	−25.824	−31.704	−37.99	−47.973	−51.611
	Na	−4.4	−15.341	−15.437	−21.246	−28.337	−36.044	−44.251	−52.878	−61.867	−71.178
Pt	Pt	−3.3	−12.412	−12.489	−17.061	−22.3	−28.083	−34.326	−40.97	−38.836	−55.299
U			−14.994	−15.088	−20.561	−26.783	−33.648	−41.095	−49.086	−57.601	−66.792
	Hg	−3.4	−22.629	−22.770	−30.795	−39.514	−48.780	−51.584			
	Al	−0.6	−8.430	−8.483	−11.699	−15.565	−19.973	−24.852	−30.150	−35.835	−42.645
	Mg	−0.4	−9.743	−9.803	−13.468	−17.790	−22.661	−28.008	−33.780	−39.937	−47.208
	Pb	−0.1	−19.316	−19.436	−26.340	−33.944	−42.122	−51.588	−61.494	−71.776	−82.389
	Sn	0.1	−15.264	−15.359	−20.911	−27.190	−35.389	−44.143	−53.304	−62.823	−72.658
	Cs	0.2	−25.387	−25.544	−35.244	−45.751	−56.887	−68.542	−80.641	−93.127	−99.241
	Y	2.2	−13.248	−13.330	−18.193	−23.742	−29.851	−36.437	−43.442	−50.824	−58.549
Rh	Rh	2.5	−9.393	−9.452	−13	−17.206	−21.958	−27.18	−32.82	−39.393	−45.199
Zn	Zn	2.9	−12.412	−12.489	−17.055	−22.283	−28.061	−34.393	−42.14	−50.28	−67.574
C			−1.712	−1.722	−2.449	−3.473	−4.789	−6.386	−8.248	−10.358	−12.7
Ag	Ag	1.5/2.4	−12.724	−12.803	−17.471	−22.79	−28.639	−34.939	−41.635	−48.684	−56.057
Au	Au	1.5/2.7	−14.161	−14.249	−19.398	−25.198	−31.525	−38.297	−45.457	−52.962	−60.779
Cu	Cu	2.0/2.6	−9.888	−9.949	−13.654	−17.998	−22.862	−28.17	−33.865	−39.904	−46.255
	W	2.5/1.5	−9.738	−9.798	−13.449	−17.729	−22.519	−27.742	−33.339	−39.271	−45.505
Cd	Cd	2.8	−15.444	−15.54	−21.132	−27.41	−34.322	−42.706	−51.516	−60.698	−70.211
	Mo	5.9	−8.525	−8.578	−11.819	−15.692	−20.084	−24.920	−30.142	−35.707	−41.583
Fe	Fe	16	−8.133	−8.184	−11.317	−15.14	−19.559	−24.513	−29.946	−35.891	−42.302
As			−10.646	−10.712	−14.674	−19.276	−24.4	−29.968	−35.924	−42.225	−48.837
Sb	Sb	35	−13.572	−13.657	−18.609	−24.216	−30.355	−36.949	−43.946	−51.31	−61.128
	Se	1000	−12.599	−12.678	−17.314	−22.738	−29.920	−37.691	−45.966	−54.682	−63.789

3.2. Molar Gibbs Free Energy and Electronegativity of 15 Typical TE Materials

Table 4 shows the G_m and X of 15 typical TE materials [31–51]. It can be seen that, in the range of 298.15~600 K, the optimal operating temperature range of Bi_2Te_3 and Sb_2Te_3 , their G_m values are between −130.196 and −248.819 kJ/mol. If these data, or $G_m = -130.196 \sim -248.819$ kJ/mol, are used as the screening criteria, it can be seen that all the above typical materials have good thermoelectric properties in a certain temperature range, indicating that the G_m of Bi_2Te_3 and Sb_2Te_3 at 298.15~600 K is feasible as the basic standard for a preliminary screening of high-thermal-power-factor thermoelectric materials.

Table 4. Temperature dependence of the G_m of typical high-performance thermoelectric materials.

Compounds	$G_m/\text{kJ/mol}$								
	298 K	300 K	400 K	500 K	600 K	700 K	800 K	900 K	1000 K
Bi_2Se_3	−211.206	−212.171	−238.210	−267.142	−298.968	−332.723	−368.406	−406.018	−445.559
Bi_2Te_3	−155.271	−155.271	−184.203	−215.064	−248.819	−285.466	−324.043		
Sb_2Se_3	−190.954	−190.954	−214.100	−241.103	−270.036	−300.897	−333.687	−369.370	−411.804
Sb_2Te_3	−130.196	−130.196	−157.199	−187.096	−219.886	−255.569	−293.182		
GeTe	−75.354	−75.521	−85.337	−96.494	−108.745	−121.928	−135.925	−150.652	
PbTe	−101.263	−101.263	−113.801	−126.338	−140.804	−156.235	−171.666	−188.061	−205.420
MnTe	−135.982	−136.947	−146.591	−158.164	−171.666	−185.167	−200.598	−216.029	−231.459
SnSe	−115.730	−115.730	−125.374	−135.982	−148.520	−161.057	−175.523	−189.989	−205.420
CoSb_3	−110.908	−110.908	−129.231	−149.484	−171.666	−196.740	−222.779	−250.747	−279.680
Cu_2Se	−104.157	−104.157	−118.623	−136.947	−156.235	−177.452	−200.598	−223.744	−247.854
Mg_2Si	−102.228	−102.228	−110.908	−121.516	−133.089	−146.591	−161.057	−176.488	−193.847
MnSi	−91.619	−91.619	−97.406	−104.157	−111.872	−120.552	−130.196	−140.804	−151.413
$\text{MnSi}_{1.7}$	−282.573	−281.609	−224.708	−193.847	−174.559	−162.986	−154.306	−149.484	−145.626
Mn_5Si_3	−284.502	−283.537	−228.566	−198.669	−180.345	−168.772	−161.057	−156.235	−152.377
FeSi_2	−97.406	−97.406	−104.157	−112.836	−122.480	−133.089	−145.626	−158.164	

Table 5 lists the electronegativity of 15 typical thermoelectric compounds calculated using Equation (16) and the electronegativity data of the elements [52–54]. It can be seen that, since the same element has different electronegativity values, the electronegativity of the corresponding compound is not unique. In addition, the electronegativity of Bi_2Te_3 and Sb_2Te_3 are very close. Considering that PbTe is a typical medium-temperature thermoelectric material, the electronegativity values of Bi_2Te_3 , Sb_2Te_3 and PbTe , that is, $X = 1.80\text{--}2.21$, are used as the criteria for screening thermoelectric materials. It can be seen that all other materials, except for Mg_2Si , have electronegativity values that meet this requirement, indicating that $X = 1.80\text{--}2.21$ is a suitable criterion.

Table 5. The electronegativity of 15 typical thermoelectric materials.

Element	X_A	X_B	A	B	X	Element	X_A	X_B	A	B	X
Bi_2Se_3	1.67	2.4	2	3	2.08	Mg_2Si	1.2	1.9	2	1	1.4
	1.67	2.1	2	3	1.92		1.2	1.74	2	1	1.36
Bi_2Te_3	1.8	2.1	2	3	1.97		1.2	1.8	2	1	1.37
	2.02	2.1	2	3	2.07		1.2	2.44	2	1	1.52
Sb_2Se_3	1.65	2.4	2	3	2.07	MnSi	1.32	2.44	2	1	1.62
	1.8	2.4	2	3	2.14		1.6	1.9	1	1	1.74
	1.82	2.4	2	3	2.15		1.6	1.74	1	1	1.67
	2.05	2.4	2	3	2.25		1.6	1.8	1	1	1.7
Sb_2Te_3	1.65	2.1	2	3	1.91	$\text{MnSi}_{1.7}$	1.6	2.44	1	1	1.98
	1.8	2.1	2	3	1.97		1.6	1.9	1	1.7	1.78
	1.82	2.1	2	3	1.98		1.6	1.74	1	1.7	1.69
	2.05	2.1	2	3	2.08		1.6	1.8	1	1.7	1.72
GeTe	1.8	2.1	1	1	1.94	Mn_5Si_3	1.6	2.44	1	1.7	2.09
	2.01	2.1	1	1	2.05		1.6	1.9	5	3	1.71
	2.02	2.1	1	1	2.06		1.6	1.74	5	3	1.65
	1.55	2.1	1	1	1.8		1.6	1.8	5	3	1.67
PbTe	1.6	2.1	1	1	1.83	FeSi_2	1.6	2.44	5	3	1.87
	1.8	2.1	1	1	1.94		1.64	1.74	1	2	1.71
	2.33	2.1	1	1	2.21		1.64	1.8	1	2	1.75
	1.4	2.1	1	1	1.71		1.64	1.9	1	2	1.81
MnTe	1.55	2.1	1	1	1.8		1.64	2.44	1	2	2.14
	1.6	2.1	1	1	1.83		1.8	1.74	1	2	1.76
SnSe	1.7	2.4	1	1	2.02		1.8	1.8	1	2	1.8
CoSb_3	1.7	2.05	1	3	1.96		1.8	1.9	1	2	1.87
Cu_2Se	1.8	2.4	2	1	1.98		1.8	2.44	1	2	2.2
FeSi_2	1.83	1.9	1	2	1.88		1.83	1.74	1	2	1.77
	1.83	2.44	1	2	2.22		1.83	1.8	1	2	1.81

3.3. Molar Gibbs Free Energy and Electronegativity of 102 Atypical TE Materials

The temperature dependences of the G_m of 102 atypical pure compounds are obtained from References [26,29]. The electronegativity X of the 102 pure atypical compounds are calculated using Equation (16). They are shown in Table 6. If $G_m = -130.196 \sim -248.819$ kJ/mol is used as the screening criterion for good TE materials, 67 compounds are screened. It can be found that, in addition to Cu_2S , Cu_2Te , Ag_2S , Ag_2Se , Ag_2Te , SnTe and PbSe , which have been widely investigated as high-performance TE materials [55–62], Bi_2S_3 , Sb_2S_3 , Mn_3Si , CoSb_2 , MoSi_2 , MnS , MnSe , MnTe_2 , FeS , FeS_2 , $\text{FeSe}_{0.96}$, $\text{FeTe}_{0.9}$, FeTe_2 , $\text{CoS}_{0.89}$, CoS_2 , $\text{NiSe}_{1.05}$, $\text{NiSe}_{1.143}$, $\text{NiSe}_{1.25}$, NiSe_2 , NiTe , $\text{NiTe}_{1.1}$, NiS_2 , NiSe_2 , CuS , InSb , GeS , GeSe , SnS , PbS , AgP_2 , AgP_3 , BeS , Be_2C , Ba_2C , AlAs , AlP , AlSb , CaC_2 , CaH_2 , CaPb , Ca_2Pb , CaSi , NaTe , NaTe_3 , NbC , NbSi_2 , InSe , CaSi_2 , Ca_2Si , CaSn , CaZn , CaZn_2 , CrS , CrSi_2 , GaP , GaSb , GaSe , GaTe , InP , InS , CuO and Cu_2O may be good TE materials at suitable temperature ranges. If the G_m of Bi_2Te_3 at a temperature of 298–800 K, or $G_m = -1.61 \sim -3.36$ eV, is used as the standard, it can be found that the other 10 compounds, namely, TiS , MoS_2 , WS_2 , MnS_2 , CoP_3 , CaTe , FeO , NiO , CdO and SnO , may be TE materials.

Table 6. The X and the temperature dependence of the G_m of atypical thermoelectric compounds.

Compounds	X	$G_m/\text{kJ/mol}$								
		298 K	300 K	400 K	500 K	600 K	700 K	800 K	900 K	1000 K
Bi_2S_3	2.19	−202.527	−203.491	−225.673	−250.747	−277.751	−308.612	−340.438	−374.192	−409.876
Sb_2S_3	2.19	−195.776	−196.740	−216.993	−240.139	−265.214	−293.182	−324.043	−359.726	−398.303
Mn_3Si	1.78	−241.103	−240.139	−193.847	−168.772	−154.306	−145.626	−139.840	−124.409	−135.018
CoSb_2	1.93	−85.833	−85.833	−99.335	−114.765	−131.160	−149.484	−169.737	−189.989	−211.206
Mg_3Sb_2	1.49	−737.776	−732.954	−574.790	−484.135	−427.235	−387.694	−360.691	−340.438	
MgSe	1.70	−1517.022	−1507.378	−1156.331	−948.983	−813.965	−718.488	−649.050	−595.043	−553.573
MgTe	1.59	−1126.435	−1119.684	−868.936	−722.345	−625.904	−558.395	−509.210	−472.562	−443.630
TiS	2.00	−288.360	−289.324	−295.110	−302.826	−311.505	−321.150	−331.758	−342.367	−353.940
TiS_2	2.15	−430.128	−431.093	−439.772	−450.381	−462.918	−476.420	−490.886	−507.281	−523.676
ZrS_2	2.11	−600.829	−600.829	−609.509	−620.118	−632.655	−646.157	−660.623	−676.054	−692.449
ZrTe_2	1.88	−330.794		−345.260		−378.050		−415.662		−458.096
TaS_2	2.03	−376.121	−376.121	−395.409	−395.409	−407.947	−421.449	−435.915	−451.345	−467.740
MoS_2	2.15	−295.110	−295.110	−301.861	−311.505	−322.114	−333.687	−346.224	−359.726	−374.192
MoSi_2	2.12	−137.911	−137.911	−145.626	−155.271	−165.879	−177.452	−190.954	−205.420	−219.886
WS_2	2.15	−278.715	−278.715	−286.431	−296.075	−306.683	−318.256			
MnS	1.87	−214.100	−214.100	−216.029	−217.957	−219.886	−220.851	−222.779	−276.787	−278.715
MnS_2	2.15	−253.641	−253.641	−265.214	−277.751	−292.217	−308.612			
MnSe	1.83	−198.669	−198.669	−208.313	−219.886	−232.424	−244.961	−259.427	−273.893	−289.324
MnTe_2	1.92	−168.772	−168.772	−185.167	−202.527	−221.815	−242.068			
FeS	2.20	−119.587	−119.587	−126.338	−135.982	−146.591	−158.164	−170.701	−184.203	−198.669
FeS_2	2.17	−187.096	−187.096	−193.847	−201.562	−211.206	−221.815	−233.388	−246.890	−260.392
$\text{FeSe}_{0.96}$	2.01	−87.762	−87.762	−95.477	−105.121	−115.730	−127.303	−140.804	−155.271	−170.701
$\text{FeTe}_{0.9}$	1.88	−47.256	−47.256	−55.936	−66.545	−77.153	−89.690	−102.228	−115.730	−130.196
FeTe_2	1.93	−102.228	−102.228	−113.801	−126.338	−141.769	−158.164	−175.523	−193.847	−199.634
$\text{CoS}_{0.89}$	2.04	−109.943	−109.943	−115.730	−123.445	−131.160	−139.840	−149.484	−160.093	−170.701
CoS_2	2.20	−173.594	−173.594	−182.274	−191.918	−202.527	−215.064	−228.566	−243.997	−259.427
CoP_3	1.99	−309.577	−309.577	−321.150	−335.616	−351.046	−369.370	−388.659	−409.876	−432.057
NiS	2.12	−103.192	−104.157	109.943	−116.694	−125.374	−135.018	−146.591	−158.164	−170.701
$\text{NiSe}_{1.05}$	2.09	−97.406	−97.406	−106.085	−115.730	−126.338	−137.911	−151.413	−164.915	−179.381
$\text{NiSe}_{1.143}$	2.10	−102.228	−103.192	−111.872	−121.516	−133.089	−145.626	−159.128	−173.594	−188.061
$\text{NiSe}_{1.25}$	2.11	−107.050	−107.050	−115.730	−126.338	−137.911	−151.413	−164.915	−180.345	−195.776

Table 6. Cont.

Compounds	X	G _m /kJ/mol								
		298 K	300 K	400 K	500 K	600 K	700 K	800 K	900 K	1000 K
NiTe	1.94	−59.794		−68.473		−89.690		−115.730		
NiTe _{1.1}	1.95	−82.940	−82.940	−92.584	−103.192	−115.730	−128.267	−141.769	−156.235	−171.666
NiS ₂	2.24	−152.377	−153.342	−161.057	−171.666	−183.238	−195.776	−210.242	−225.673	−241.103
NiSe ₂	2.18	−139.840	−139.840	−151.413	−164.915	−180.345	−196.740	−215.064	−233.388	−253.641
CuS	2.18	−73.295	−73.295	−80.046	−88.726	−98.370	−108.979	−120.552	−132.125	−144.662
Cu ₂ S	2.01	−115.730	−115.730	−129.231	−145.626	−162.986	−183.238	−204.456	−226.637	−248.819
Cu ₂ Te	1.89	−81.975	−81.975	−97.406	−113.801	−133.089	−154.306	−176.488	−201.562	−226.637
Ag ₂ S	2.01	−75.224	−76.189	−91.619	−109.943	−130.196	−151.413	−174.559	−197.705	−222.779
Ag ₂ Se	1.98	−82.940	−82.940	−99.335	−120.552	−142.733	−166.843	−191.918	−217.957	−244.961
Ag ₂ Te	1.89	−81.975	−81.975	−98.370	−118.623	−141.769	−164.915	−189.989		
ZnSb	1.84	−43.399	−43.399	−53.043	−63.651	−75.224	−86.797	−100.299		
InSb	1.91	−55.936	−55.936	−65.580	−76.189	−88.726	−101.263	−114.765	−135.018	−156.235
GeS	2.12	−95.477	−95.477	−103.192	−111.872	−121.516	−132.125	−143.698	−155.271	−169.737
GeSe	2.08	−92.584	−92.584	−101.263	−110.908	−122.480	−134.053	−146.591	−160.093	−175.523
PbS	2.00	−126.338	−126.338	−135.982	−140.804	−159.128	−172.630	−186.132	−200.598	−216.029
PbSe	1.90	−130.196	−131.160	−141.769	−154.306	−167.808	−182.274	−196.740	−212.171	−228.566
SnS	2.06	−131.160	−131.160	−139.840	−149.484	−160.093	−171.666	−184.203	−197.705	−212.171
SnTe	1.89	−91.619	−91.619	−103.192	−114.765	−128.267	−142.733	−157.199	−172.630	−189.025
AgP ₂	1.99	−69.438	−69.438	−80.046	−91.619	−105.121	−119.587	−135.018	−152.377	
AgP ₃	2.02	−101.263	−101.263	−113.801	−128.267	−145.626	−163.950	−185.167	−207.349	
BeS	1.94	−244.961	−244.961	−249.783	−254.605	−261.356	−268.107	−276.787	−285.466	−294.146
Be ₂ C	1.83	−121.516	−121.516	−124.409	−127.303	−132.125	−136.947	−143.698	−150.448	−157.199
BaC ₂	2.11	−101.263	−101.263	−110.908	−122.480	−135.982	−149.484	−164.915	−181.310	−198.669
AlAs	1.82	−134.053	−134.053	−140.804	−149.484	−158.164	−167.808	−178.416	−189.025	−200.598
AlI ₃	2.20	−359.726	−359.726	−380.943	−395.409					
AlP	1.84	−178.416	−758.993	−184.203	−190.954	−197.705	−205.420	−215.064	−223.744	−233.388
Al ₂ S ₃	2.04	−758.993	−758.993	−772.495	−788.890	−808.178	−828.431	−851.577	−875.687	−901.726
Al ₂ Se ₃	1.99	−613.367	−613.367	−630.726	−650.979	−674.125	−699.200	−726.203	−755.136	−785.032
AlSb	1.82	−69.438	−69.438	−77.153	−85.833	−94.512	−105.121	−115.730	−127.303	−139.840
BaS	1.50	−483.171	−484.135	−491.851	−502.459	−513.068	−524.641	−537.178	−550.680	−564.182
CaC ₂	1.84	−81.011	−81.011	−88.726	−98.370	−109.943	−122.480	−135.982	−151.413	−166.843
CaH ₂	1.64	−189.025	−189.025	−193.847	−200.598	−207.349	−215.064	−223.744	−232.424	−243.032
CaPb	1.53	−144.662	−145.626	−154.306	−163.950	−175.523	−188.061	−200.598	−215.064	−229.530
Ca ₂ Pb	1.33	−243.997	−244.961	−256.534	−270.036	−284.502	−300.897	−318.256	−336.580	−355.868
CaS	1.58	−489.922	−489.922	−496.673	−504.388	−513.068	−522.712	−532.356	−543.929	−555.502
CaSi	1.56	−164.915	−164.915	−169.737	−176.488	−183.238	−191.918	−200.598	−210.242	−220.851
CaSe	1.55	−387.694	−388.659	−395.409	−404.089	−413.733	−424.342	−435.915	−447.488	−460.025
NaTe	1.46	−199.634	−199.634	−208.313	−218.922	−230.495				
NaTe ₃	1.75	−165.879	−165.879	−181.310	−198.669	−218.922	−240.139			
NbC	2.06	−149.484	−149.484	−153.342	−159.128	−164.915	−171.666	−179.381	−188.061	−196.740
NbSi ₂	2.16	−146.591	−146.591	−154.306	−163.950	−175.523	−188.061	−200.598	−215.064	−230.495
InSe	1.90	−142.733	−142.733	−151.413	−162.021	−172.630	−185.167	−198.669	−212.171	
CaSi ₂	1.81	−165.879	−165.879	−172.630	−180.345	−189.989	−200.598	−212.171	−224.708	−238.210
Ca ₂ Si	1.35	−233.388	−233.388	−243.032	−253.641	−266.178	−280.644	−295.110	−311.505	−328.865
CaSn	1.40	−180.345	−180.345	−188.061	−196.740	−207.349	−217.957	−230.495	−242.068	−255.569
CaTe	1.45	−315.363	−316.328	−324.043	−333.687	−344.295	−354.904	−366.477	−379.014	−391.552

Table 6. Cont.

Compounds	X	G_m /kJ/mol								
		298 K	300 K	400 K	500 K	600 K	700 K	800 K	900 K	1000 K
CaZn	1.28	−92.584	−93.548	−100.299	−108.979	−119.587	−130.196			
CaZn ₂	1.40	−124.409	−124.409	−135.982	−149.484	−163.950	−180.345	−197.705	−216.993	
CrS	1.87	−174.559	−174.559	−182.274	−190.954	−199.634	−210.242	−221.815	−234.352	−246.890
CrSi ₂	2.12	−116.694	−116.694	−123.445	−131.160	−140.804	−151.413	−162.986	−175.523	−189.025
GaP	1.95	−115.730	−115.730	−121.516	−128.267	−136.947	−145.626	−155.271	−164.915	−176.488
GaSb	1.93	−64.616	−64.616	−72.331	−81.011	−89.690	−99.335	−109.943	−119.587	
GaSe	2.08	−180.345	−180.345	−188.061	−196.740	−207.349	−217.957	−229.530	−242.068	−255.569
GaTe	1.95	−148.520	−149.484	−158.164	−168.772	−180.345	−192.883	−206.384	−220.851	−235.317
InP	1.93	−106.085	−107.050	−113.801	−121.516	−130.196	−139.840	−150.448	−161.057	−172.630
InS	2.11	−154.306	−154.306	−162.021	−171.666	−181.310	−191.918	−203.491	−216.029	−230.495
Ag ₂ O	2.25	−67.509	−67.509	−81.011	−95.477					
MgFe ₂ O ₄	2.48	−1474.588		−1490.018		−1528.595		−1577.780		−1635.645
CaTiO ₃	2.33	−1688.687	−1688.687	−1699.296	−1713.762	−1729.193	−1747.517	−1767.769	−1789.951	−1813.097
CaZrO ₃	2.30	−1796.702	−1796.702	−1808.275	−1822.741	−1839.136	−1858.424	−1878.677	−1900.858	−1924.004
SrTiO ₃	2.33	−1705.082	−1705.082	−1717.620	−1733.050	−1750.410	−1770.663	−1791.880	−1815.026	−1839.136
Mn ₂ O ₃	2.49	−992.381	−992.381	−1004.919	−1020.349	−1037.709	−1057.961	−1079.178	−1102.324	−1127.399
FeO	2.40	−290.288	−290.288	−297.039	−305.719	−314.399	−325.007	−335.616	−347.189	−359.726
Fe ₃ O ₄	2.53	−1162.118	−1162.118	−1179.477	−1200.694	−1226.734	−1255.666	−1287.492	−1323.175	−1360.787
Fe ₂ O ₃	2.58	−850.612	−850.612	−861.221	−874.723	−890.153	−909.442	−929.694	−951.876	−976.951
CuO	2.47	−168.772	−168.772	−173.594	−180.345	−187.096	−194.811	−203.491	−213.135	−222.779
Cu ₂ O	2.20	−198.669	−198.669	−208.313	−220.851	−234.352	−248.819	−264.249	−280.644	−298.004
NiO	2.47	−250.747	−250.747	−255.569	−263.285	−268.107	−276.787	−285.466	−295.110	−304.755
ZnO	2.29	−363.584	−363.584	−368.406	−375.157	−381.908	−389.623	−398.303	−407.947	−417.591
CdO	2.29	−274.858	−275.822	−281.609	−289.324	−297.039	−306.683	−316.328	−326.936	−338.509
SnO	2.44	−302.826	−302.826	−309.577	−317.292	−325.972	−335.616	−346.224	−356.833	−368.406

If $X = 1.80\sim 2.21$ is used as the screening criterion of high-performance TE materials, 67 compounds are screened out. A comparison of the screening results of the two methods shows that their results are not completely consistent, although most of them are. For compounds that meet the G_m screening criteria, the main difference is reflected in alkali metal and alkaline earth metal compounds. These compounds, such as the alkali metal compounds NaTe and NaTe₂ and the alkaline earth metal compounds CaH₂, CaPb, Ca₂Pb, CaSi, Ca₂Si, CaSn, CaTe, CaZn and CaZn₂, are less electronegative than the screening criteria. The X value of some transition metal compounds, such as Mn₃Si, is also lower than the screening criterion. Transition metal oxides or sulfides, such as FeO, CuO, NiO, CdO, SnO and NiS₂, have a larger X value than the screening criteria due to the high electronegativity of O or S. Therefore, although they have TE properties, they are not very good TE materials. So, a bigger X is not better. If both G_m and X are met as screening criteria, a total of 60 pure compounds have the potential to become high-quality TE materials. They are Cu₂S, Cu₂Te, Ag₂S, Ag₂Se, Ag₂Te, SnTe, Bi₂S₃, Sb₂S₂, CoSb₂, TiS, MoS₂, MoSi₂, WS₂, MnS, MnSe, MnTe₂, FeS, FeS₂, FeSe_{0.96}, FeTe_{0.9}, FeTe₂, CoS_{0.89}, CoS₂, CoP₃, NiS, NiSe_{1.05}, NiSe_{1.143}, NiSe_{1.25}, NiSe₂, NiTe_{1.1}, NiS₂, NiSe₂, CuS, InSb, GeS, GeSe, SnS, PbS, AgP₂, AgP₃, BeS, Be₂C, Ba₂C, AlAs, AlP, AlSb, CaC₂, NbC, NbSi₂, InSe, CaSi₂, CrS, CrSi₂, GaP, GaSe, GaTe, InP, InS and Cu₂O.

3.4. Molar Gibbs Free Energy (G_m) and Electronegativity of Some Potential TE Materials

Based on the above G_m and X criteria, 44 possible high-performance thermoelectric compounds are screened directly from the pure substance thermochemical data book [29]. Their electronegativity values are calculated according to Formula (16). The results are presented in Table 7. There are several compounds, such as GeS₂, MgB₄, Mo₃Si, OsSe₂, Pd₄S, PtBr₂, PtI₄ and ReS₂, whose electronegativity values deviate from the screening criteria.

Table 7. The X and the temperature dependence of the G_m of some potential TE compounds.

Compounds	X	G_m /kJ/mol								
		298	300	400	500	600	700	800	900	1000
GeS ₂	2.24	−182.972	−183.134	−192.925	−204.453	−217.428	−231.658	−247.008	−263.375	−280.682
GeSe	2.08	−92.363	−92.509	−101.125	−111.046	−122.039	−133.951	−146.673	−160.125	
GeSe ₂	2.18	−146.525	−146.733	−159.119	−173.371	−189.166	−206.292	−224.597	−243.967	−264.315
InTe	1.94	−103.476	−103.672	−114.999	−127.581	−141.202	−155.719	−171.031	−187.063	
In ₂ Te	1.94	−125.861	−126.148	−142.706	−161.059	−180.918	−202.091			
IrS ₂	2.13	−153.634	−153.762	−161.728	−171.474	−182.705	−195.21	−208.836	−223.457	−239.01
MgB ₄	1.62	−120.499	−120.595	−126.939	−135.278	−145.367	−157.024	−170.113	−184.525	−200.173
Mn ₇ C ₃	1.83	−180.432	−180.875	−208.533	−242.455	−281.592	−325.235	−372.878	−424.138	−478.719
Mn ₄ N	1.81	−171.263	−171.528	−187.866	−207.711	−230.506				
MnP	1.83	−132.428	−132.549	−139.843	−148.441	158.131	−168.751	−180.179	−192.23	−205.1
MnTe ₂	1.92	−168.757	−169.026	−184.752	−202.457	−221.747	−242.362			
Mo ₂ N	1.97	−100.425	−100.524	−107.912	−117.106	−127.873	−140.024	−153.411	−167.92	−183.458
MoSi ₂	2.12	−138.21	−138.331	−145.876	−155.167	−165.905	−177.882	−190.944	−204.972	−219.876
Mo ₃ Si	1.78	−133.356	−133.554	−145.65	−160.148	−176.604	−194.726	−214.306	−235.189	−257.255
NbC _{0.702}	1.99	−126.67	−126.729	−130.466	−135.13	−140.577	−146.704	−153.431	−160.699	−168.459
NbC _{0.825}	2.02	−134.083	−134.144	−138.012	−142.865	−148.549	−154.954	−161.993	−169.602	−177.729
NbSi ₂	2.16	−146.353	−146.482	−154.5	−164.221	−175.344	−187.665	−201.037	−215.349	−230.514
Ni ₃ Sn	1.84	−132.871	−133.115	−147.837	−165.181	−184.701	−206.103	−229.177	−253.766	
Ni ₃ Sn ₂	1.86	−208.67	−208.991	−228.08	−250.01	−274.284	−300.573	−328.641	−358.316	−389.461
OsP ₂	2.07	−176.748	−176.9	−186.225	−197.386	−210.04	−223.964	−238.996	−255.017	−271.933
OsSe ₂	2.26	−144.406	−144.558	−153.754	−164.629	−176.842	−190.157	−204.405	−219.456	−235.21
PdI ₂	2.04	−116.886	−117.219	−136.408	−157.551	−180.296	−204.414	−229.74		
PdS ₂	2.04	−104.438	−104.601	−114.449	−126.078	−139.192	−153.58	−169.089	−185.602	−203.028
Pd ₄ S	2.09	−122.901	−123.236	−143.131	−166.052	−191.482	−219.081	−248.607	−279.88	−312.759
PtBr ₂	2.24	−116.346	−116.445	−122.991	−131.511	−141.651	−153.177	−165.924		
PtI ₄	2.24	−126.692	−127.027	−147.125	−170.65	−197.119	−226.212			
PtS ₂	2.08	−132.725	−132.864	−141.394	−151.706	−163.501	−176.571	−190.762	−205.958	−222.065
ReS ₂	2.24	−196.745	−196.858	−203.987	−212.896	−223.29	−234.958	−247.748	−261.542	−276.248
ReSi ₂	2.20	−112.454	−112.591	−121.029	−131.188	−142.771	−155.57	−169.433	−184.245	−199.912
Re ₂ Te ₅	2.01	−169.237	−169.704	−197.679	−230.246	−266.6	−306.209	−348.694	−393.774	−441.228
RuSe ₂	2.01	−185.827	−185.979	−195.29	−206.502	−219.273	−233.369	−248.618	−264.893	−282.093
Ta ₂ Si	1.92	−156.956	−157.151	−168.802	−182.292	−197.3	−213.601	−231.031	−249.465	−268.806
TaSi ₂	2.16	−135.905	−136.01	−142.703	−151.174	−161.121	−172.329	−184.638	−197.924	−212.09
TiSi	2.04	−144.299	−144.39	−150.02	−156.89	−164.797	−173.598	−183.187	−193.483	−204.421
TiSi ₂	2.16	−152.519	−152.632	−159.805	−168.782	−179.278	−191.085	−204.051	−218.057	−233.01
USi ₂	2.02	−154.154	−154.306	−163.677	−175.054	−188.12	−202.635	−218.415	−235.315	−253.222
VSi ₂	2.13	−168.213	−168.323	−175.267	−183.976	−194.162	−205.616	−218.183	−231.744	−246.204
WSi ₂	2.12	−112.088	−112.207	−119.641	−128.798	−139.381	−151.181	−164.054	−177.858	−192.528
ZrSi	1.91	−172.148	−172.256	−178.783	−186.49	−195.17	−204.68	−214.918	−225.803	−237.276
ZrSi ₂	2.07	−180.742	−180.874	−189.059	−198.947	−210.238	−222.727	−236.266	−250.746	−266.078
SmC ₂	1.94	−122.441	−122.604	−132.522	−144.333	−157.717	−172.445	−188.346	−205.292	−223.18
TaC	2.06	−156.734	−156.812	−161.656	−167.544	−174.326	−181.884	−190.128	−198.986	−208.402
ZnSe	2.00	−179.949	−180.08	−187.926	−197.097	−207.337	−218.474	−230.388	−242.988	−256.205
ZnTe	1.87	−142.447	−142.591	−151.162	−161.036	−171.984	−183.858	−196.552	−209.987	−224.099

3.5. The Procedure for the High-Throughput Screening of TE Materials with Gibbs Free Energy and Electronegativity

Because the molar Gibbs free energy of a compound is easily found in the thermochemical data book or calculated, and its electronegativity is easily calculated using the geometric mean value of Mulliken electronegativity, the potential of a material as a high-performance thermoelectric material can be easily and quickly determined. In order to facilitate the screening of TE materials using molar Gibbs free energy (G_m) and electronegativity (X), a schematic diagram of the screening process is shown in Figure 1.

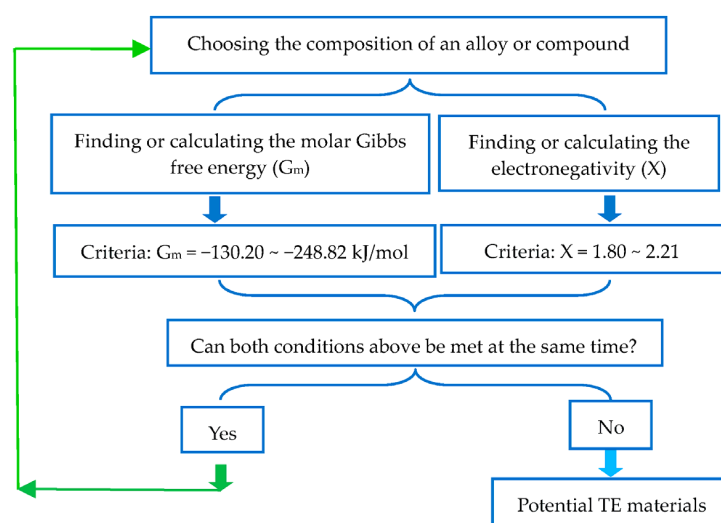


Figure 1. Flowchart for screening high-performance of TE materials using molar Gibbs free energy (G_m) and electronegativity (X).

Additionally, one problem should be discussed. From the results of the analysis of the whole paper, the only typical TE compound that cannot meet the requirements of $G_m = -130.20 \sim -248.82$ kJ/mol and $X = 1.80 \sim 2.21$ at the same time is Mg_2Si . That is, its X does not meet the requirements because the electronegativity of the element Mg is too low. But why can Mg_2Si become a typical thermoelectric material? The first reason is that the G_m of Mg_2Si meets the requirements. The second reason is that X can meet the requirements by changing its composition, which is also the strategy adopted in the research process of Mg_2Si TE materials. Therefore, when screening thermoelectric materials, G_m data can be used as the main data, supplemented by X data. It is a reasonable improvement strategy to adjust the composition of a TE material so that its X value meets the requirements.

4. Conclusions

Screening high-performance thermoelectric materials and improving their thermoelectric properties are important goals of thermoelectric materials research. Based on the objective relationship among the molar Gibbs free energy (G_m), the chemical potential, the Fermi level, the electronegativity (X) and the TE property of a material, a new method using molar Gibbs free energy (G_m) and electronegativity (X) for the high-throughput screening of thermoelectric materials is proposed. The molar Gibbs free energy of 15 typical TE materials, 9 widely studied thermoelectric materials and 93 atypical thermoelectric materials were obtained from a thermochemical data book. The electronegativities of the materials above were calculated using the geometric mean value of Mulliken electronegativity. The feasibility of using G_m and X as high-throughput screening thermoelectric materials is discussed in detail. The results are described below.

1. Because it is universal that Fermi levels and scattering factors have a decisive effect on the thermoelectric properties of materials, taking the molar Gibbs free energy G_m and electronegativity X as screening criteria for high-performance TE materials is reasonable.

2. The molar Gibbs free energy G_m s of typical TE materials Bi_2Te_3 and Sb_2Te_3 range from -130.196 to -248.819 kJ/mol. The electronegativity X s of Bi_2Te_3 , Sb_2Te_3 and $PbTe$ range from 1.80 to 2.21. If $G_m = -130.20 \sim -248.82$ kJ/mol and $X = 1.80 \sim 2.21$ are used as screening criteria for high-performance TE materials, the G_m and X of all of 15 typical TE materials and 9 widely studied thermoelectric materials meet the requirements very well, except for the X of Mg_2Si . It is indicated that $G_m = -130.20 \sim -248.82$ kJ/mol and $X = 1.80 \sim 2.21$ are suitable criteria for screening high-performance TE materials.

3. For TE materials, such as Mg_2Si , due to the extremely low electronegativity of the component elements, its X value cannot meet the requirements, but its G_m can meet the requirements very well. G_m data can be used as the main data, supplemented by X data. It is a reasonable improvement strategy to adjust the composition of a TE material so that its X value meets the requirements.

4. For good TE compounds, if G_m and X are required to meet the corresponding standards at the same time, and $G_m = -130.196 \sim -248.819$ kJ/mol and $X = 1.80 \sim 2.21$ are used as screening criteria, 60 pure substances, including 9 widely studied TE materials, are screened as potential TE materials from 102 atypical TE materials.

5. With reference to their electronegativity, 44 pure substances are selected directly from the thermochemical data book as potential high-performance thermoelectric materials. A particular finding is that several carbides, such as Be_2C , CaC_2 , BaC_2 and NbC , may have certain TE properties.

6. Compared with $G_m = -130.196 \sim -248.819$ kJ/mol, the elemental elements in the Seebeck or Meissner sequence are not good thermoelectric materials. This is consistent with the actual results.

7. The G_m of pure substances can be easily found in thermochemical data books, and the X of compounds can be calculated easily from the X of pure elements, so using G_m and X as high-throughput screening criteria for predicting thermoelectric properties is much more convenient than using the TE figure of merit Z or ZT or the Ab initio calculation method. This method requires no experiments and no first principle or Ab initio calculation.

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