



Model to determine thermal conductivity at high pressure and temperature

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Abstract. In the present study, the thermal conductivity relation equation given by Leibfried and Schlomann is extended and thermal conductivity is estimated at different pressures and temperatures by predicting the variation of Debye temperature, Gruneisen parameter and volume compression with temperature and pressure. The change in volume under variable pressure and temperature for the materials considered, viz. NaCl, NaI, KCl and KBr, are predicted from Goyal–Gupta pressure–volume–temperature equation. The results obtained for variation of volume with temperature and pressure using Goyal–Gupta equation are compared with the available experimental data and theoretical values obtained using Stacey’s equation. The thermal conductivity values are estimated at different temperatures with pressure along different isotherms and results are compared with thermal conductivity data available in previous studies for pressure dependence as well as for temperature dependence to justify the present model.

Keywords. Thermal conductivity; pressure; temperature; Debye temperature.

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1. Introduction

The behaviour of solids under high pressure and temperature has been emerged as an interdisciplinary area of research because of its widespread applications in areas of physics, chemistry, biology, material sciences, engineering and technology. Such studies result in the discovery of various novel phenomena and provide new insight to study the behaviour of solids [1, 2]. The physical properties of solids are found modified under the effect of temperature because of the modification in the interatomic distance of atoms and molecules. Temperature can modify the physical properties of materials and also lead to the creation of new materials [3, 4].

Thermal conductivity, an important thermal property of solids, plays an important role in geophysical investigations and shock temperature measurements. Determination of the thermal conductivity of materials in the Earth’s interiors is necessary to understand the thermal behaviour along with the dynamics of the core and mantle regions. It is very difficult to determine the experimental values of thermal conductivity at elevated pressures and temperatures because of the complexities involved [5, 6]. For theoretical determination

of thermal conductivity, we must know the thermoelastic properties of solids along with the dependence of Gruneisen parameter γ and Debye temperature θ on pressure and temperature. It is evident from the previous studies that shock temperature measurements and geophysical investigations can be done by measuring thermal conductivity at high pressures and temperatures [7–12].

To determine the thermodynamic properties theoretically, an equation of state (EoS) is required. An EOS expresses the relation between the thermodynamic variables such as pressure, temperature, volume, internal energy, etc. It is of great importance in solid-state physics to determine the thermo-elastic properties of solids. Extrapolated data can be obtained using EoS in the region where the experimental values are not available. The isothermal EoS is used to determine the volume compression, bulk modulus, its high-pressure derivatives, etc. of solids at variable pressures. The isobaric EoS helps to determine the volume expansion, bulk modulus, etc. of solids at variable temperatures [13, 14].

Many theoretical models have been developed to estimate the thermal conductivity of solids but very few of them can find the values at high temperatures and

pressures. A fundamental equation to estimate the thermal conductivity at variable pressures and temperatures is given by Leibfried *et al* [15] according to which thermal conductivity depends on Debye temperature, Gruneisen parameter, lattice parameter and the number of atoms in a cell in a solid. Tang [16] presented the extended form of Leibfried–Schlomann relation to obtain thermal conductivity values at high pressures and temperatures. Sharma *et al* [17] used the Stacey equation [18, 19] and Shankar equation [20, 21] to determine the pressure and temperature effect on thermoelastic properties of solids. Further, the thermal conductivity is determined using the Tang model.

In the present study, isothermal and isobaric forms of Goyal and Gupta EoS [22–24] are used to compute the volume compression under pressure and volume expansion under temperature for alkali halides as the EoS considered is adequate in the high-pressure region. The variation of Debye temperature with pressure at different temperatures is estimated using the relation given by Hama and Suito [25]. To determine the variation of Gruneisen parameter with pressure at variable temperatures, the relation given by Stacey [26] is used.

2. Method of analysis

The fundamental relation to determine thermal conductivity in non-metallic crystals given by Leibfried and Schlomann [15] is as follows:

$$K = cn^{1/3} \frac{aM\theta^3}{\gamma^2 T}, \quad (1)$$

where c is a constant, n represents the number of atoms per cell, a ; M represent lattice parameter and average atomic weight, θ ; γ represent the Debye temperature and Gruneisen parameter at temperature T .

To determine the relative change in thermal conductivity at high temperatures and pressures, $K(T, P)/K(T_0, P)$, Tang [16] has extended the Leibfried–Schlomann relation as follows:

$$\frac{K(T, P)}{K(T_0, P)} = \frac{a}{a_0} \left[\frac{\theta(T, P)}{\theta(T_0, 0)} \right]^3 \left[\frac{\gamma(T, P)}{\gamma(T_0, 0)} \right]^{(-2)} \left[\frac{T}{T_0} \right]^{-1}, \quad (2)$$

where parameter with subscript 0 indicates a normal state, i.e., at room temperature and atmospheric pressure.

Expressing lattice parameter in terms of volume V , eq. (2) can be written as [16]

$$\frac{K(T, P)}{K(T_0, P)} = \left[\frac{V(T, P)}{V(T_0, 0)} \right]^{1/3} \left[\frac{\theta(T, P)}{\theta(T_0, 0)} \right]^3$$

$$\times \left[\frac{\gamma(T, P)}{\gamma(T_0, 0)} \right]^{(-2)} \left[\frac{T}{T_0} \right]^{-1}. \quad (3)$$

To compute the thermal conductivity, pressure–volume relation formulated by Goyal and Gupta [22] at room temperature T_0 is used which is given as follows:

$$P(V, T_0) = B_0 \left(\frac{V_0}{V} - 1 \right) + \frac{B_0(B'_0 - 1)}{2} \times \left(\frac{V_0}{V} - 1 \right)^2. \quad (4)$$

Here V/V_0 represents the volume compression at room temperature and pressure P ; B_0 , B'_0 represent bulk modulus and its first-order pressure derivative at $P = 0$.

Bulk modulus B obtained using eq. (1) is expressed as follows [22]:

$$B = \frac{V_0}{V} \left[B_0 + B_0(B'_0 - 1) \left(\frac{V_0}{V} - 1 \right) \right]. \quad (5)$$

Equation (4) in terms of V/V_0 at pressure P and room temperature T_0 can be written as follows [23]:

$$\left(\frac{V(T_0, P)}{V(T_0, 0)} \right)^{-1} = 1 + \frac{\{B_0^2 + 2B_0P(V, T_0)(B'_0 - 1)\}^{1/2} - B_0}{B_0(B'_0 - 1)}. \quad (6)$$

Differentiation of bulk modulus B with respect to P gives B'_P , which is expressed as follows [24]:

$$B'_P = \frac{dB}{dP} = \frac{V_0}{VB} B_0 \left[1 + (B'_0 - 1) \left(2 \frac{V_0}{V} - 1 \right) \right]. \quad (7)$$

In eq. (7), V in the denominator represents the volume at some pressure P and B stands for the bulk modulus. At temperature T , total pressure acting on the solid including thermal pressure P_{Th} can be expressed as [2]

$$P(V, T) = P(V, T_0) + P_{Th}, \quad (8)$$

where

$$P_{Th} = \int_{T_0}^T \alpha B dT = \alpha B(T - T_0). \quad (9)$$

T_0 and T stand for room temperature and elevated temperature, respectively. α_0 and α represent thermal expansion coefficients at T_0 and T , respectively.

To consider the effect of both temperature and pressure on volume, the relative change in volume is expressed as

$$\frac{V(T, P)}{V(T_0, 0)} = \frac{V(T_0, P)}{V(T_0, 0)} \frac{V(T, P)}{V(T_0, P)}. \quad (10)$$

In view of eqs (6)–(10), expression of $\frac{V(T,P)}{V(T_0,0)}$ can be obtained as follows [23, 24]:

$$\left(\frac{V(T,P)}{V(T_0,P)}\right)^{-1} = 1 + \frac{\{B_0^2 + 2B_0(P(V,T) - \alpha B(T - T_0))(B'_0 - 1)\}^{1/2} - B_0}{B_0(B'_0 - 1)}. \tag{11}$$

The present computed results for thermal conductivity are compared with the results obtained using the Tang model [16].

The variation of Debye temperature with pressure at selected temperatures is obtained using the relation given as follows [25]:

$$\frac{\theta(T,P)}{\theta(T_0,0)} = \left(\frac{V(T_0,P)}{V(T_0,0)}\right)^{1/6} \left[\frac{B}{B_0} - \frac{4P}{3B_0}\right]^{1/2}. \tag{12}$$

The variation of Gruneisen parameter with pressure at selected temperatures is evaluated using the relation given by Stacey [26]:

$$\gamma(T,P) = \frac{B'_P}{2} - \frac{1}{6} - \frac{\frac{f}{3}\left(1 - \frac{B'_P}{B}P\right)}{1 - \frac{2fP}{3B}}. \tag{13}$$

At $P = 0$,

$$\gamma(T,0) = \frac{B'_0}{2} - \frac{1}{6} - \frac{f}{3}. \tag{14}$$

Considering eqs (13) and (14), for $f = 2$, the ratio $\gamma(T,P)/\gamma(T,0)$ is given by

$$\frac{\gamma(T,P)}{\gamma(T,0)} = \frac{\left\{\frac{B'_P}{2} - \frac{1}{6} - \frac{\frac{2}{3}\left(1 - \frac{B'_P}{B}P\right)}{1 - \frac{4P}{3B}}\right\}}{\left(\frac{B'_0}{2} - \frac{5}{6}\right)}. \tag{15}$$

Considering the pressure–volume–temperature relation (eq. (11)) along with the relation for variation of Gruneisen parameter (eq. (15)) and Debye temperature (eq. (12)) with pressure at different temperatures, thermal conductivity is determined in the present work.

The pressure dependence of thermal conductivity at room temperature is given by Tang [16] using the relation as follows:

$$\frac{K(P)}{K(0)} = \left(1 + \frac{B'_0 P}{B_0}\right)^{5B'_0/3} \times \exp\left[3\gamma_0 \left\{1 - \left(1 + \frac{B'_0 P}{B_0}\right)\right\}^{-1/B'_0}\right]. \tag{16}$$

The temperature dependence of thermal conductivity at zero pressure is given by Tang [16] using the relation as follows:

$$\frac{K(T)}{K(T_0)} = \left[\frac{T}{T_0}\right]^{-1} \frac{\exp[-3\gamma_0\alpha(T - T_0)]}{[1 + \alpha(T - T_0)]^{5/3}}. \tag{17}$$

3. Results and discussion

In the present study, pressure–volume–temperature relation obtained using Goyal and Gupta EoS, i.e. eq. (11), is used to compute volume compression under pressure and volume expansion under temperature for alkali halides, i.e. NaCl, KCl, NaI, KBr. Goyal and Gupta EoS [24] is found to be thermodynamically consistent at boundary conditions as $B = B_0$; $B' = B'_0$ when $P = 0$; $V = V_0$ and also at high pressures, it follows Stacey’s criteria well. The equation used to compute the pressure and temperature dependence of volume in alkali halides is applicable in the high-pressure region and its validity is justified using Stacey’s criteria [22–24]. To determine the variation of Gruneisen parameter with pressure at different temperatures, eq. (15) given by Stacey [26] is used. The variation of Debye temperature with pressure at different temperatures is estimated using eq. (12). The combined effect of temperature and pressure on thermal conductivity is evaluated by incorporating eqs (11), (12) and (15) in Leidfried–Schlomann relation (eq. (2)) in the present study. The input parameters are listed in table 1.

The reason for choosing alkali halides which are non-metallic crystals in the present study is that the study of thermal conduction in solids helps us to investigate thermodynamic processes in Earth. The present model is applicable for non-metallic crystals. In the present study, alkali halides are considered because the experimental data for comparing the present model results is available in literature at different pressures and temperatures.

The results obtained for the variation of volume with temperature and pressure $V(T,P)/V(T,0)$ from the present EoS are compared with the results obtained by Sharma *et al* [17] as listed in table 2 for NaCl and KCl at temperatures 300, 500, 700 and 900 K. It is clear from table 2 that variation of volume with temperature and pressure from the present EoS are in good accordance with the previous results obtained from the Stacey equation.

The dependence of thermal conductivity on pressure at room temperature for NaCl, KCl, NaI and KBr is evaluated using eq. (13) and the obtained results are

Table 1. Input parameters at room temperature and zero pressure [13, 16, 17].

Material	B_0 (GPa)	B'_0	α (10^{-5} K^{-1})	$\gamma(T_0, 0)$	K_0 (W/mK)
NaCl	24.0	5.35	11.8	1.91	5.95
KCl	17.0	5.5	1.11	1.5	6.40
NaI	16.2	5.99	13.7	3.18	1.33
KBr	14.8	6.03	1.0	1.5	2.9

Table 2. $V(T, P)/V(T_0, 0)$ obtained using the present EoS (eq. (7)) and Stacey's EoS [17].

NaCl P (GPa)	300 K (eq. (7))	300 K Ref. [17]	500 K (eq. (7))	500 K Ref. [17]	700 K (eq. (7))	700 K Ref. [17]	900 K (eq. (7))	900 K Ref. [17]
0	1.00	1.00	1.0255	1.0259	1.0564	1.0580	1.0963	1.1000
0.538	0.9791	0.9791	1.0011	1.0014	1.0268	1.0279	1.0580	1.0580
1.22	0.9560	0.9562	0.9748	0.9752	0.9962	0.9970	1.0210	1.0201
2.08	0.9309	0.9311	0.9469	0.9472	0.9646	0.9651	0.9846	0.9831
3.20	0.9030	0.9035	0.9165	0.9169	0.9311	0.9314	0.9471	0.9457
4.68	0.8721	0.8732	0.8832	0.8842	0.8951	0.8959	0.9079	0.9071
6.67	0.8378	0.8397	0.8468	0.8485	0.8564	0.8578	0.8665	0.8664
9.44	0.7992	0.8027	0.8064	0.8097	0.8139	0.8168	0.8217	0.8234
11.2	0.7785	0.7826	0.7849	0.7887	0.7915	0.7949	0.7984	0.8005
13.4	0.7557	0.7615	0.7613	0.7668	0.7670	0.7721	0.7730	0.7770
16.1	0.7314	0.7389	0.7362	0.7434	0.7411	0.7479	0.7462	0.7521
19.4	0.7057	0.7151	0.7098	0.7188	0.7140	0.7228	0.7184	0.7263
23.6	0.6779	0.6897	0.6813	0.6929	0.6849	0.6961	0.6885	0.6990
29.0	0.6478	0.6626	0.6507	0.6652	0.6537	0.6678	0.6567	0.6702
KCl								
P (GPa)								
0	1.0	1.0	1.0240	1.0236	1.0527	1.0534	1.0888	1.0911
0.380	0.9791	0.9791	0.9998	0.9995	1.0238	1.0243	1.0524	1.0525
0.860	0.9561	0.9562	0.9739	0.9736	0.9939	0.9941	1.0169	1.0161
1.48	0.9306	0.9311	0.9457	0.9458	0.9623	0.9626	0.9808	0.9700
2.26	0.9032	0.9035	0.9159	0.9158	0.9297	0.9296	0.9446	0.9433
3.31	0.8723	0.8732	0.8827	0.8832	0.8939	0.8944	0.9059	0.9052
4.73	0.8379	0.8397	0.8462	0.8478	0.8552	0.8566	0.8647	0.8649
6.69	0.7991	0.8027	0.8059	0.8090	0.8130	0.8159	0.8203	0.8222
7.97	0.7779	0.7826	0.7839	0.7882	0.7901	0.7941	0.7965	0.7996
9.50	0.7556	0.7615	0.7608	0.7663	0.7662	0.7715	0.7718	0.7762
11.4	0.7314	0.7389	0.7359	0.7430	0.7406	0.7474	0.7454	0.7514
13.7	0.7061	0.7151	0.7100	0.7186	0.7140	0.7223	0.7181	0.7243
16.7	0.6780	0.6897	0.6813	0.6926	0.6846	0.6957	0.6881	0.6983
20.4	0.6489	0.6626	0.6516	0.6651	0.6544	0.6676	0.6572	0.6698

compared with those of Tang (eq. (16)) [16] as shown in figures 1a–1d. An increase in thermal conductivity with an increase in pressure can be observed in figure 1. Tang [16] developed empirical relations depicting the variation of thermal conductivity with an increase in pressure and temperature using the experimental data [6]. Therefore, in the present work comparison is done with the Tang model results. Good accordance is found between the compared results from figures 1a and 1b which justify the present model. The trend of variation is the same for the results depicted in figures 1c and 1d

for NaI and KBr. The experimental data of the variation of thermal conductivity with pressure for KBr is taken from ref. [27].

It is noted that in non-metallic diatomic crystals, the heat transport is mainly due to phonons, viz. acoustic phonons and optical phonons. The contribution of optical phonons is important only in diatomic solids in which the ionic mass ratio is almost unity. For NaI, the mass ratio is 5.52 [6] which reduces the impact of optical phonons. The large mass ratio in NaI may also affect the volume dependence of thermal conductivity.

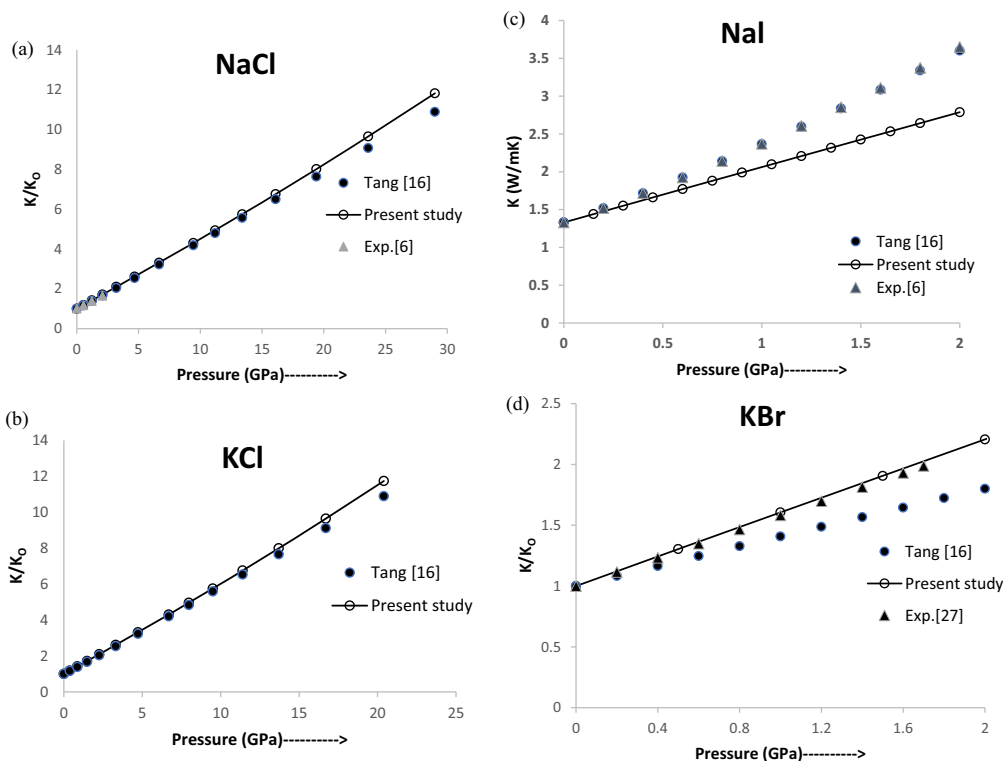


Figure 1. Thermal conductivity vs. pressure in (a) NaCl, (b) KCl, (c) NaI and (d) KBr at room temperature.

Also, the value of Gruneisen parameter at zero pressure γ_0 is taken from literature in Tang model while in the present model, the relative value of Gruneisen parameter $\gamma(T, P)/\gamma(T, 0)$ is calculated at different pressures using the relation given by Stacey (eq. (15)). This may be the reason for the deviation of the present model results from the available experimental values. Tang model is an approximation relation to depict the pressure and temperature dependence of thermal conductivity of non-metallic crystals.

Figure 1d depicts the variation of thermal conductivity with pressure in KBr. From the graph, it can be seen that experimental results [27] are in good agreement with the present model results in comparison with the Tang model results.

Further, the dependence of thermal conductivity on the temperature at zero pressure for NaCl is evaluated using eq. (13) and the obtained results are compared with those of Tang (eq. (17)) as shown in figure 2a. The thermal conductivity is found to decrease as temperature increases at zero pressure. Figures 2a–2d depict the variation in thermal conductivity with temperature for NaCl, KCl, NaI and KBr at zero pressure. It is noted from figures 2a–2d that thermal conductivity decreases with an increase in temperature. There is good agreement between the compared results [6, 16] which

indicate that the present model can predict well the thermal conductivity of solids at variable pressures and temperatures.

Figure 3a depicts the variation of thermal conductivity with an increase in pressure for NaCl, at temperatures 300, 500, 700 and 900 K. It is noted from figure 3 that thermal conductivity decreases as temperature increases. Figure 3b depicts the variation in thermal conductivity with temperature for NaCl at pressures 0, 5, 10 and 15 GPa, respectively. An increase in thermal conductivity with an increase in pressure is noticed more at room temperature and as temperature increases, there is a substantial drop in the increase of thermal conductivity. The opposite trend in thermal conductivity with pressure and temperature matches well with the trend of variation of thermal conductivity as in the previous studies. The isothermal variation of thermal conductivity is just the reverse of isobaric variation. A good accordance between the compared results is observed.

It is known that in non-metallic solids, viz. alkali halides, thermal transport or heat is carried by quantised lattice vibrations called phonons. The thermal conductivity is found to decrease with an increase in temperature in alkali halides due to the anharmonic scattering. In non-metallic solids, as temperature increases,

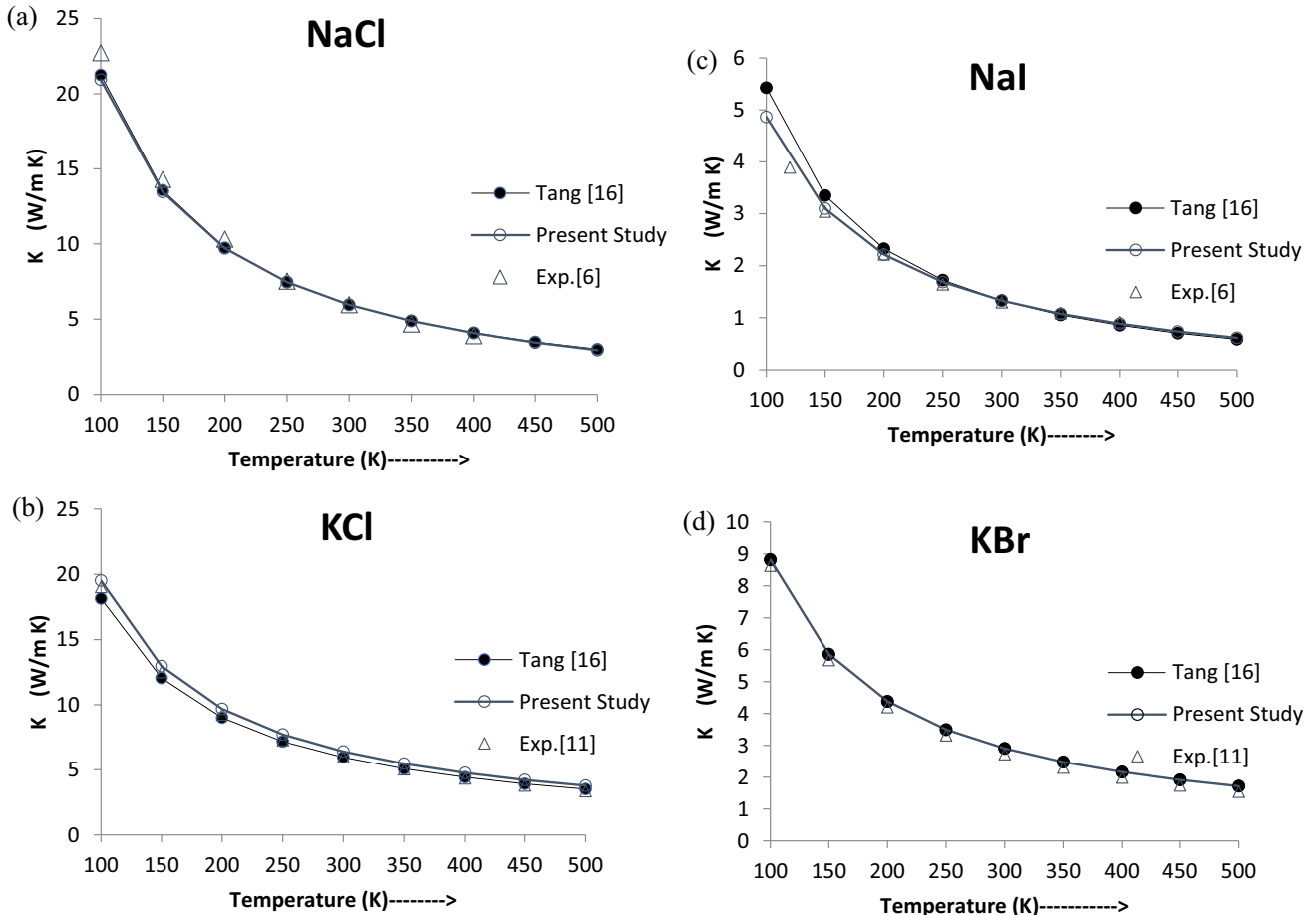


Figure 2. Thermal conductivity vs. temperature in (a) NaCl, (b) KCl, (c) NaI and (d) KBr.

the flow of electrons is hindered due to the distortions of the network causing a decrease in thermal conductivity.

In non-metallic solids, thermal conductivity is found to increase with pressure because as pressure increases, particles in the solids come closer and collision between the particles takes place which increases the phonon frequencies and group velocities of the material leading to an increase in thermal conductivity.

In many solids, depending on their atomic structure, a phase transformation may take place at high pressure which will affect all thermal transport properties.

Previously, the Tang model had been used to determine the thermal conductivity in non-metallic solids. Tang used the pressure–volume equation, viz. Bridgman’s equation and Murnaghan’s equation of state which are valid only at low pressures. In the Tang model, the equation used to represent the volume dependence of the Gruneisen parameter is not valid if the volume changes are considerable. Also, the equation

that represents the volume–temperature relation in the Tang model is not valid at high temperatures [16]. Thus, it can be said that the Tang model is not adequate for solids at high pressures and high temperatures. The empirical relations developed by previous workers to determine the thermal conductivity dependence on pressure and temperature in non-metallic crystals are based on certain approximations where higher-order terms with pressure and temperature are neglected [6, 16].

4. Conclusion

The model explains well the variation of thermal conductivity with pressure and temperature which is very difficult to determine experimentally. The present model does not involve any approximation and the present results match well with the previously available results which support the validity of the present model

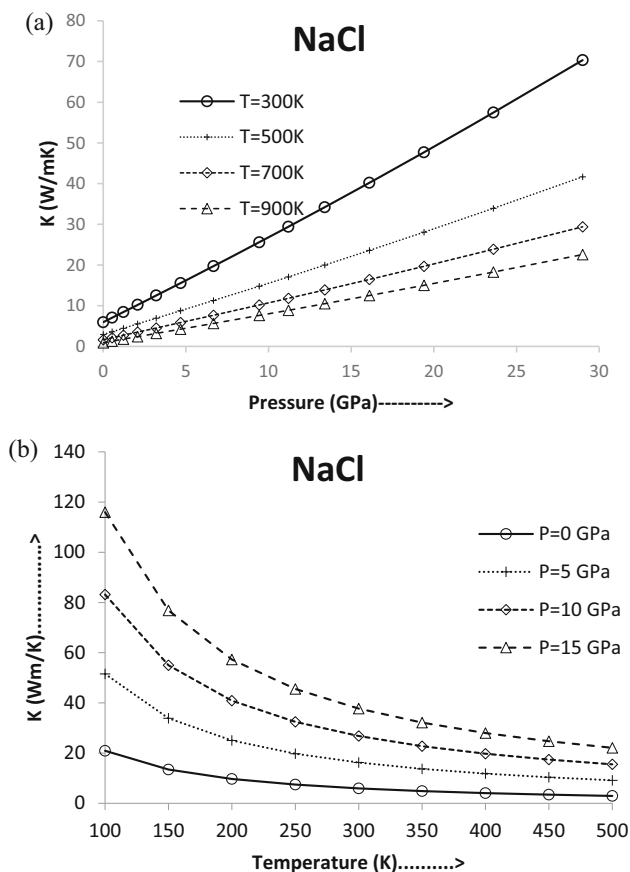


Figure 3. (a) Thermal conductivity vs. pressure in NaCl at different temperatures and (b) thermal conductivity vs. temperature in NaCl at different pressures.

theory. The present study can provide good insight for researchers involved in experimental studies.

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