Thermal Expansivity and Isothermal Bulk Modulus of Various Classes of Minerals at High Temperatures

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In this paper, a new expression for temperature dependence of thermal expansivity and bulk modulus are developed using a simple thermodynamical equation of state. The proposed equation of state is applied to investigate the study thermal expansivity and bulk modulus of various classes of minerals and provides the non-linear models for variation of both thermal expansivity and bulk modulus with temperatures. The results obtained for various earth's minerals are discussed and compared with experimental results. The computed values of thermal expansivity and bulk modulus have shown a good agreement with available experimental results. It is concluded that a new expression for thermal expansivity and bulk modulus is capable to predict the elastic properties of Earth's minerals under high temperature conditions.

Keywords: EOS, Thermal expansivity, Bulk modulus, Minerals.

1. INTRODUCTION

The study of elastic properties of minerals is essential for examining and understanding of the dynamics of earth's deep interior, structure and composition of earth's lower mantle and in seismic studies [1]. The elasticity offers more information than the volume in interpreting the temperature dependence of equation of state (EOS) because the compressibility is defined by the derivative of volume. Thermal expansivity is a very important parametric quantity for interpreting the thermodynamic and thermo elastic behaviour of minerals at high temperatures because it has been emphasized [2] that most of the serious errors in the calculations of thermodynamic functions arise due to uncertainty of thermal expansivity at high temperatures. The behaviours of elastic properties under the effect of high pressure and high temperature have attracted the attention of experimental [3-5] as well as theoretical workers [6-9].

The equation of state is basically a pressure-volume-temperature relationship. The studies based on EOS are widely important not only in physics but also in chemistry and geophysics [3-8]. The theoretical studies of EOS at different pressures and temperatures are of fundamental interest as they permit interpolation and extrapolation to the region in which the experimental data are not available. The present study describes the theoretical study of thermoelastic properties especially compression, thermal expansion, bulk modulus, and thermal expansion coefficient of various classes of minerals. The relation between pressure and volume at constant temperature is known as isothermal EOS while the relation between temperature and volume at constant pressure is known as isobaric EOS. In the present communication, we have also considered a empirical form of δ_T as a function of temperature and obtained other expressions to calculate the thermal expansion coefficients and bulk modulus of various classes of minerals. The computed values of the thermal expansion coefficients and bulk modulus have shown a good agreement with available experimental results [1,3] and far better than the earlier theoretical studies [8,10-13].

2. THEORY

One of the most widely used thermodynamic approximations is that product αK_T remains constant [14], i.e.

$$\alpha K_T = \text{Constant.} \tag{1}$$

Where α and K_T are the coefficient of volume thermal expansion and isothermal bulk modulus, respectively

On differentiating Eq. (1) with respect to T, at constant pressure, we have

$$\alpha \left(\frac{dK_T}{dT} \right)_P + K_T \left(\frac{d\alpha}{dT} \right)_P = 0 \tag{2}$$

Or
$$\left(\frac{dK_T}{dT} \right)_P = -\frac{K_T}{\alpha} \left(\frac{d\alpha}{dT} \right)_P \tag{3}$$

The isothermal Anderson-Grüneisen parameter δ_T is defined as follows [15]

$$\delta_T = -\frac{1}{\alpha K_T} \left(\frac{\partial K_T}{\partial T} \right)_P \tag{4}$$

Substituting the value of Eq. (3) in Eq. (4), we get

$$\delta_T = \frac{1}{\alpha^2} \left(\frac{\partial \alpha}{\partial T} \right)_P \tag{5}$$

Where α is the coefficient of volume thermal expansion and defined as follows

$$\alpha = -\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \tag{6}$$

From of Eq. (5) and Eq. (6), we get

$$\delta_T = \frac{V}{\alpha} \left(\frac{\partial \alpha}{\partial V} \right)_P \tag{7}$$

The empirical temperature dependence of δ_T is considered as follows [16]

$$\delta_T = \delta_T^0 (X)^k \tag{8}$$

Where δ_T^0 is the value of Anderson-Grüneisen parameter at $T = T_0$ and $X = T/T_0$, T_0 is the reference temperature and *k* is the new dimensionless parameter which can be calculated from the slope of the graph plotted between $\log \delta_T^0$ and $\log(T/T_0)$. If we thus substitute the value of δ_T from Eq. (8) in Eq. (5), we can be obtained the modified expression for thermal expansion coefficient as follows

$$\delta_T^0 X^k = \frac{1}{\alpha^2}\left(\frac{\partial \alpha}{\partial T}\right)_P \tag{9}$$

Or

$$\delta_T^0 \left(\frac{T}{T_0}\right)^k = \frac{1}{\alpha^2}\left(\frac{\partial \alpha}{\partial T}\right)_P \tag{10}$$

By integrating Eq. (10), we have

$$\frac{\delta_T^0}{T_0^k}\frac{T_0^{k+1}}{(k+1)} = -\frac{1}{\alpha_T} + C \tag{11}$$

Where C is an integration constant evaluated from initial conditions at $T = T_0$ and $\alpha_T = \alpha_0$,

$$\frac{\delta_T^0}{T_0^k (k+1)}(T^{k+1} - T_0^{k+1}) = \frac{1}{\alpha_0} - \frac{1}{\alpha_T} \tag{12}$$

The final expression for thermal expansivity is thus obtained as

$$\frac{\alpha_T}{\alpha_0} = \left[1 - \frac{\alpha_0 \delta_T^0}{T_0^k (k+1)}(T^{k+1} - T_0^{k+1})\right]^{-1} \tag{13}$$

If the empirical temperature dependence of δ_T is assumed then Eq. (4) at P = 0, may also written as follows

$$-\left(\frac{\partial K_T}{\partial T}\right)_P = \alpha_0 K_0 \delta_T \tag{14}$$

Using Eq.(8), we have

$$\delta_T^0 \left(\frac{T}{T_0} \right)^k = -\frac{1}{\alpha_0 K_0} \left(\frac{\partial K_T}{\partial T} \right)_P \tag{15}$$

Integrating Eq. (15), we have

$$\int_{K_0}^{K_T} dK_T = -\alpha_0 K_0 \delta_T^0 \int_{T_0}^{T} \left(\frac{T}{T_0} \right)^k dT \tag{16}$$

Thus, we get the final expression for the bulk modulus K_T is

$$K_T = K_0 \left[1 - \frac{\alpha_0 \delta_T^0}{T_0^k (k+1)} (T^{k+1} - T_0^{k+1}) \right] \tag{17}$$

Where K_{T0} is the value of K_T at initial temperature $T = T_0 = 300K$ and at atmospheric pressure.

3. RESULT AND DISCUSSIONS

In the present paper, we have calculated the temperature dependence of thermal expansion and bulk modulus, using Eqs. (13) and (17) respectively with their explanations. This EOS is entirely free from the use of potentials and needs only three input parameters such as Anderson Grunesian parameter (δ_T^0), volume thermal expansion coefficient (α_0) at zero pressure and reference temperature, and thermoelastic parameter *k* which can be calculated from the graph between $\log(\delta_T^0)$ and $\log(T/T_0)$ as represented by Eq. (8) [1]. The values of *k* may also obtained by curve fitting method. Its value is found 0.11, 0.19, 0.012, 0.09 and 0.102 for MgO, NaCl, KCl, Al_2O_3 and Mg_2SiO_4 respectively. The values of input parameters are given in the Table 1, along with the other parameters required for present computation [3].

Table 1: Values of input parameters [3], α_0 in ($10^{-5}K^{-1}$), K_0 (in GPa), *k* and δ_0 (dimensionless).

Minerals	α_0	K_0	δ_0	*K*
MgO	3.12	161.1	5.26	0.11
NaCl	11.8	24	5.2	0.19
KCl	11.0	17	5.84	0.012
Al_2O_3	1.62	252	6.96	0.09
Mg_2SiO_4	2.72	127.3	5.94	0.102

The variation of volume thermal expansivity (α_T) and bulk modulus (K_T) of these minerals i.e. MgO, NaCl, KCl, Al_2O_3 and Mg_2SiO_4 respectively, are shown in Figures 1 and 2, together with available experimental data [1,3] for the sake of comparison of our results. The maximum deviations are found at the highest temperatures. We have therefore calculated the percentage deviations of bulk modulus for each mineral at highest temperatures and reported in Table 2. It is found in each case that our calculated values are in very close agreement with the available experimental data [1,3]. Figures 1(a) and 1(b) explain the variation of volume thermal expansivity (α_T) with varying temperature for NaCl and KCl respectively.

Table 2: Percentage deviations at highest temperatures using present theory for which the experimental data are available.

MgO	**NaCl**	**KCl**	**Al_2O_3**	**Mg_2SiO_4**
T = 1800 K	T = 750 K	T = 850 K	T = 750 K	T = 1800 K
K_T = 0.17	K_T = 1.0	K_T = 0.45	K_T = 0.15	K_T = 0.17

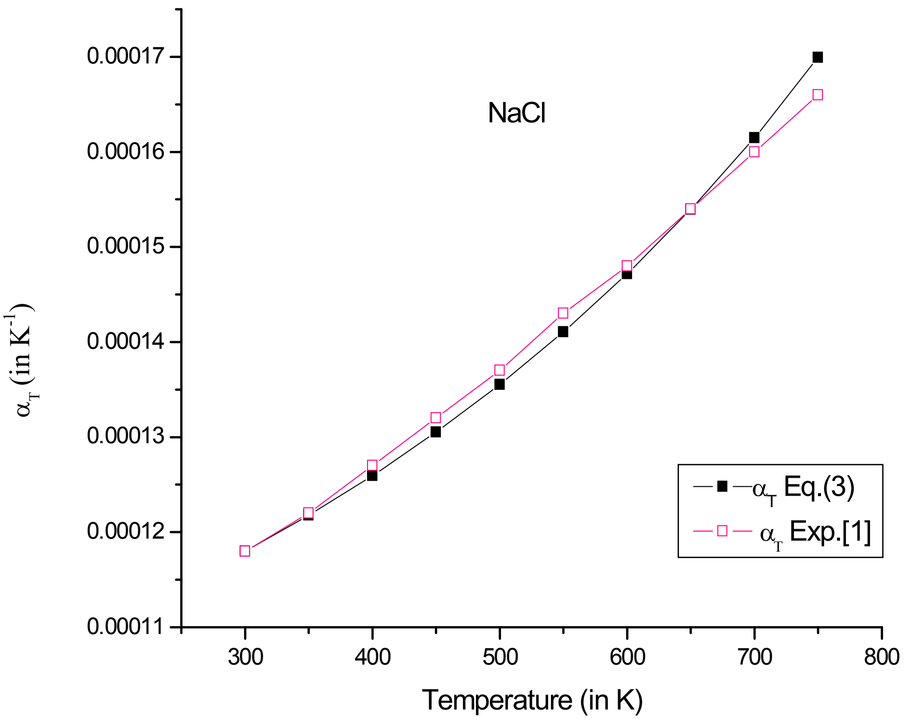


Fig. 1(a): Thermal expansion coefficient Vs temperature for NaCl.

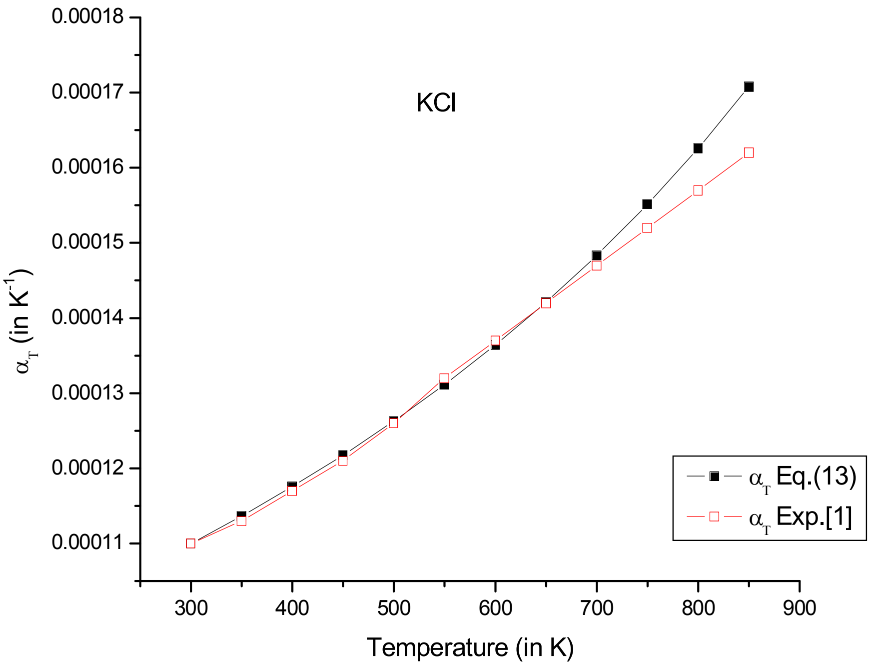
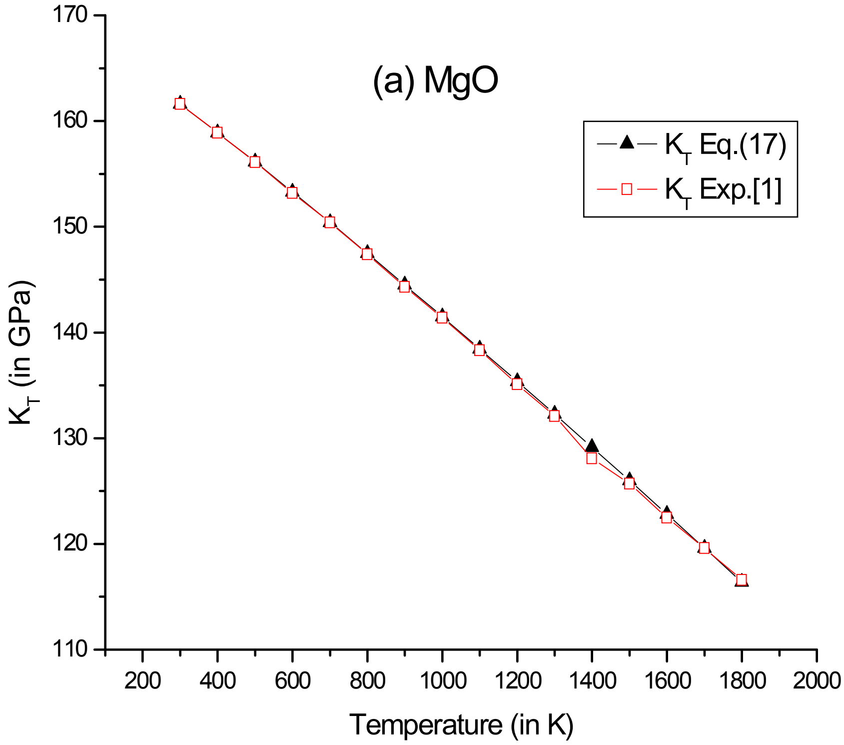
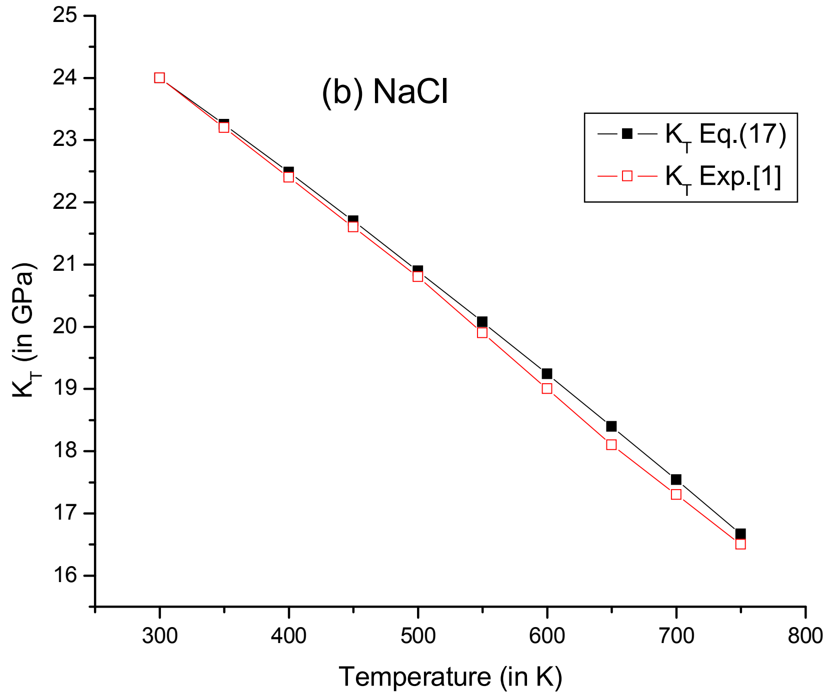


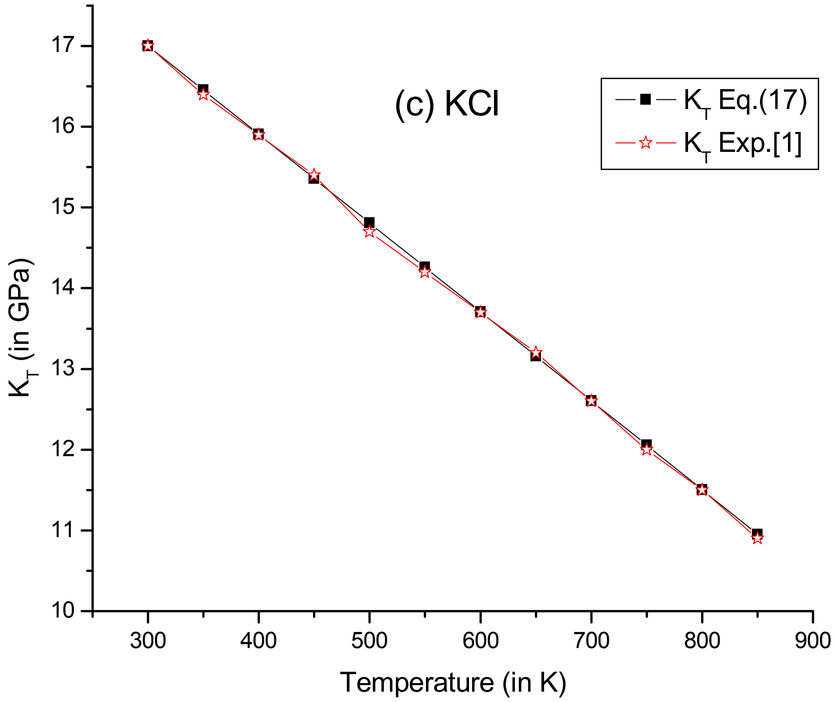
Fig. 1(b): Thermal expansion coefficient Vs temperature for KCl.

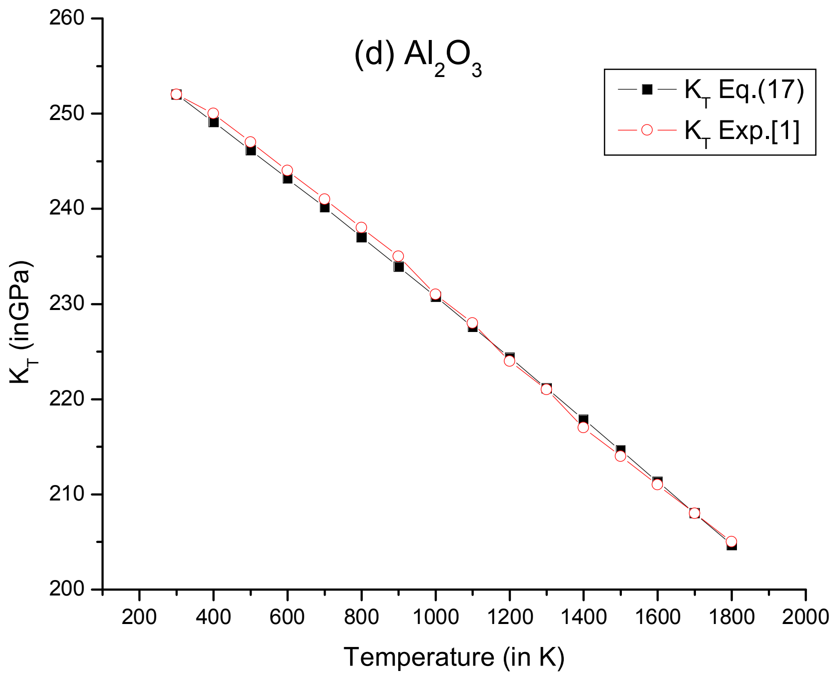
The results of the variation of bulk modulus (K_T) with temperature obtained from Eq. (17) are plotted in Figures 2(a), 2(b), 2(c), 2(d) and 2(e) for various classes of minerals i.e. MgO, NaCl, KCl, Al_2O_3 and Mg_2SiO_4 respectively.

The Figures 1(a) and (b) expose that the volume thermal expansion show increasing trend with increase of temperature and are very close to experimental data [1]. Thus the obtained results by Eq. (13) show the validity of these equations and proposed model is superior to other theoretical models [11-12,17-19]. The Figures 2(a) to 2(e) show decreasing trend with increase of temperature. On the other hand the values of bulk modulus are in excellent agreement with the experimental values [1] at different temperature and are superior to other theoretical models [8-14,17-18]. This proves the melting theory according to which $K_T \rightarrow 0$ as $T \rightarrow T_m$. Thus the obtained results by Eq. (17) show the validity of these equations and also prove the validity of proposed EOS.


(a) MgO
K_T Eq.(17)
K_T Exp.[1]
K_T (in GPa)
Temperature (in K)
170
160
150
140
130
120
110
200
400
600
800
1000
1200
1400
1600
1800
2000


(b) NaCl
K_T Eq.(17)
K_T Exp.[1]
K_T (in GPa)
Temperature (in K)
25
24
23
22
21
20
19
18
17
16
300
400
500
600
700
800


(c) KCl
K_T Eq.(17)
K_T Exp.[1]
K_T (in GPa)
Temperature (in K)


(d) Al2O3
K_T Eq.(17)
K_T Exp.[1]
K_T (inGPa)
Temperature (in K)

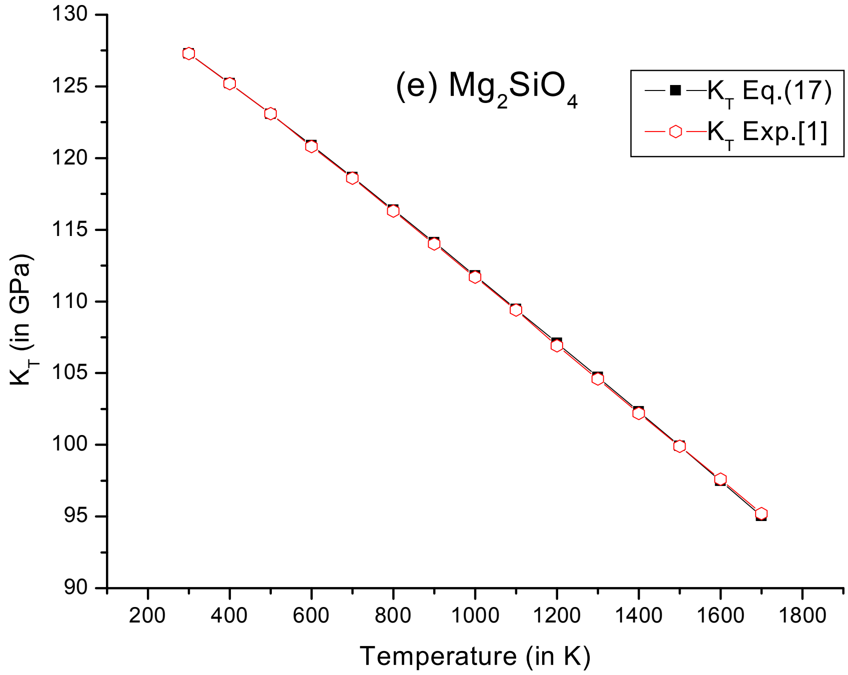


Fig. 2: Temperature variation of bulk modulus (K_T) for (a) MgO, (b) NaCl, (c) KCl, (d) Al_2O_3 and (e) Mg_2SiO_4.

We have thus presented a simple and straightforward method, so far to study the elastic properties for ionic solids under varying conditions of temperature. The results obtained are demonstrated that the present method is far better as compared with earlier studies [7-14,16-19]. It can be extended to more complex solids like minerals of geophysical importance and applications.

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