

Temperature Dependence of Elastic Constants for Ionic Solids

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Abstract: A simple and straightforward theoretical model is developed to investigate the elastic constants for ionic solids under the effect of temperature. The calculation are performed with the help of high temperature equation of state (EOS) derived from Tallon's method based on thermodynamic analysis. The results obtained for ionic solids are discussed and compared with experimental data under the effect of high temperature. The results are found to be in good agreement with available experimental results and thus may be helpful in analyzing the other's experimental results.

Keywords: EOS; SOEC; ionic Solids.

1. Introduction

The ceramic science requires the knowledge of temperature dependence of elastic properties of materials. The knowledge of temperature dependence of elastic moduli is of central importance for understanding the thermo elastic behaviour of solids in high temperature region. 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 ¹. The behaviors of elastic constants under the effect of high pressure and high temperature have attracted the attention of experimental ²⁻⁴ as well as theoretical workers ⁵⁻⁸. It has been observed that the theoretical methods are divided into two categories: (i) Interionic potential based methods. Which are very tedious ⁵⁻⁸ and involve heavy computational work in addition to various approximations ⁵⁻⁸. (ii) Potential independent methods. The potential independent methods have several advantages and simple over the interionic potential based methods.

There are based on the less approximation, easy to handle, structure ind-

ependent, and require less input data. These are particularly important for complicated solids like minerals, because of the fact that for minerals it becomes very difficult to write the potential of concerning minerals. Thus it may be useful to propose a simple and straightforward method is developed to investigate the elastic constants for ionic solids under the effect of temperature.

2. Theory

The isothermal Anderson-Grüneisen parameter δ_T is defined as follows ⁹

$$(2.1) \quad \delta_T = - \frac{1}{\alpha B_T} \left(\frac{\partial B_T}{\partial T} \right)_P,$$

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

By definition, the coefficient of volume thermal expansion

$$(2.2) \quad \alpha = - \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P,$$

and isothermal bulk modulus is defined as follows:

$$(2.3) \quad B_T = \frac{1}{V} \left(\frac{\partial P}{\partial V} \right)_T,$$

A method has been developed to estimate the temperature dependence of bulk modulus with the approximation that α depends linearly or quadratically on the temperature ¹⁰. But we find that, in case of NaCl whose experimental results has been reported, the values of B_T calculated by Kumar ¹⁰ and Liu et al. ¹¹ is adequate for small expansions. Thus, the approximation that α depends linearly or quadratically on temperature is valid only for small expansions that are low temperature range. Through comparing and analyzing some experimental data, the present communication puts forward that α depends third polynomial of temperature, which can be written as follows:

$$(2.4) \quad \alpha = \alpha_0 + \alpha_0' (T - T_0) + \frac{\alpha_0''}{2!} (T - T_0)^2 + \frac{\alpha_0'''}{3!} (T - T_0)^3.$$

Where α_0 is the value of α at T_0 . α'_0 , α''_0 and α'''_0 are respectively, the first, second and third order temperature derivatives of α at initial temperature $T = T_0 = 300K$. One of the most widely used thermodynamic approximation¹² is that product αB_T remains constant, then using equation (2.1), we have

$$(2.5) \quad \delta_T = \frac{1}{\alpha^2} \left(\frac{\partial \alpha}{\partial T} \right)_P,$$

Assuming δ_T to be independent of T [12], we can get the following relations

$$(2.6) \quad \alpha'_0 = \left(\frac{\partial \alpha}{\partial T} \right)_P = \delta_{T_0} \alpha_0^2,$$

$$(2.7) \quad \alpha''_0 = \left(\frac{\partial^2 \alpha}{\partial T^2} \right)_P = 2 \delta_{T_0}^2 \alpha_0^3,$$

and

$$(2.8) \quad \alpha'''_0 = \left(\frac{\partial^3 \alpha}{\partial T^3} \right)_P = 6 \delta_{T_0}^3 \alpha_0^4,$$

Where δ_{T_0} is the value of δ_T at T_0 and atmospheric pressure, i.e. at $P = 0$. Therefore equation (2.4) can be written as follows:

$$(2.9) \quad \alpha = \alpha_0 + \delta_{T_0} \alpha_0^2 (T - T_0) + \delta_{T_0}^2 \alpha_0^3 (T - T_0)^2 + \delta_{T_0}^3 \alpha_0^4 (T - T_0)^3.$$

Substituting the value of α from equation (2.9) in equation (2.1), we have

$$(2.10) \quad \frac{dB_T}{B_T} = -\delta_{T_0} [\alpha_0 + \delta_{T_0} \alpha_0^2 (T - T_0) + \delta_{T_0}^2 \alpha_0^3 (T - T_0)^2 + \delta_{T_0}^3 \alpha_0^4 (T - T_0)^3] dT.$$

Integrating equation (2.10), thus the following expression for bulk modulus $B_T(T)$:

$$(2.11) \quad \frac{B_T}{B_{T_0}} = \exp \left(-\delta_{T_0} \alpha_0 (T - T_0) \left(1 + \frac{\delta_{T_0} \alpha_0 (T - T_0)}{2} + \frac{\delta_{T_0}^2 \alpha_0^2 (T - T_0)^2}{3} + \frac{\delta_{T_0}^3 \alpha_0^3 (T - T_0)^3}{4} \right) \right)$$

where B_{T_0} is the value of B_T at initial temperature $T = T_0 = 300 K$ and at atmospheric pressure. Grover et al.¹³ used a non-standard definition¹⁴ of δ_T known as isothermal Anderson-Grüneisen parameter and recalled it the parameter g as given as below:

$$(2.12) \quad g = - \frac{V_0}{B_T} \left(\frac{\partial B_T}{\partial V} \right)_P,$$

where V_0 is the value of V at $P = 0$. Equation (2.12) when generalized read as follows:

$$(2.13) \quad g_M = - \frac{V_0}{M} \left(\frac{\partial M}{\partial V} \right)_P,$$

where M represent any of the elastic moduli, such as $C_{11}, C_{12}, C_{44}, (C_{11} - C_{12})/2$ or B_T . Tallon [14] has expressed equation (2.13) as follows:

$$(2.14) \quad \frac{M}{M_0} = \exp \left(-g_M \left(\frac{V}{V_0} - 1 \right) \right),$$

Equation (2.14) may be used to determine the temperature dependence of elastic constants. Following the method of generalization as used by Tallon¹⁴ to get equation (2.14), we can generalize equation (2.11) as follows:

$$(2.15) \quad \frac{M}{M_0} = \exp \left(-\delta_{M_0} \alpha_0 (T - T_0) \left(1 + \frac{\delta_{M_0} \alpha_0 (T - T_0)}{2} + \frac{\delta_{M_0}^2 \alpha_0^2 (T - T_0)^2}{3} + \frac{\delta_{M_0}^3 \alpha_0^3 (T - T_0)^3}{4} \right) \right)$$

In equation (2.15), δ_{M_0} should vary according to elastic moduli selected. On the basis of equation (2.15), the relevant expression for elastic constants may be written collectively as follows:

$$(2.16) \quad \frac{C_{ij}}{C_{ij0}} = \exp \left[-\delta_{ij0} \alpha_0 (T - T_0) \left(1 + \frac{\delta_{ij0} \alpha_0 (T - T_0)}{2} + \frac{\delta_{ij0}^2 \alpha_0^2 (T - T_0)^2}{3} + \frac{\delta_{ij0}^3 \alpha_0^3 (T - T_0)^3}{4} \right) \right].$$

Here δ_{ij0} is given by equation (2.1) and evaluated from the definition of δ , using the following relation

$$(2.17) \quad \delta_{0ij} = -\frac{1}{\alpha_0 C_{ij0}} \left(\frac{\partial C_{ij}}{\partial T} \right)_P.$$

Thus, if the measurement has been made at a temperature close to the room temperature for C_{ij} , the values of δ_{ij0} may be evaluated.

3. Result and Discussions

The values of input parameters have been calculated for ionic solids using the data reported by Anderson and Isaak² in the Table-1 along with the other parameters required for present computation². The Eq. (2.11), obtained by the authors, is used to compute the values of B_T at different T , using input data² given in Table-1. The results obtained are reported in Figures 1 to 4 along with experimental data² for comparison. In all cases i.e. MgO, CaO, NaCl and KCl, it has been found that Eq.(2.11) improves the results as compared the other theoretical results [7,15-18] and good agreement with the experimental results². The maximum deviations are found at highest temperatures. We have therefore calculated the percentage deviations at highest temperatures and reported in Table 2. In all cases, the deviations are less.

Table-1: Values of input parameters [2]. α_0 in (10^{-5}K^{-1}), δ_0 (dimensionless).

Parameters	MgO	CaO	NaCl	KCl
α_0	3.12	3.04	11.8	11.0
δ_0	5.3	6.19	5.2	5.84
δ_{011}	6.27	7.31	6.28	7.48
δ_{012}	-2.49	-2.0	0.051	-3.31
δ_{044}	2.57	2.88	2.35	3.04

Thus, Eq. (2.11) proposed by the authors seems to suitable for the temperature dependence of bulk modulus. This encouraged the authors to extend Eq. (2.11) for the study of the variation of elastic moduli. Equation (2.11) may be generalized in the form of Eq. (2.15). Equation (2.15) may be written for the second-order elastic constants (SOEC) in the form of Eq. (2.16) which is used to compute the temperature dependence of SOEC of ionic solids. The results thus obtained are given in Figures 1 to 4 along with the experimental data [1-2]. The results obtained for the elastic constants for these solids under study present reasonably good agreement with the available experimental data [1-2]. The percentage deviations calculated at highest temperatures are reported in Table 2. The variation of C_{11} with temperature is found to be larger as compared with C_{12} and C_{44} . The constant C_{11} represent elasticity in length. A longitudinal strain produces a change in volume without a change in shape. The volume change is highly related to the temperature and thus produces a large change in C_{11} . On the other hand, the constants C_{12} and C_{44} are related to the elasticity in shape which is shear constant.

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

MgO T = 1800 K	C_{11} 1.6	C_{12} 13.31	C_{44} 3.83	B_T 4.23	NaCl T = 750 K	C_{11} 2.01	C_{12} 2.01	C_{44} 0.81	B_T 5.33
CaO T = 1200 K	C_{11} 0.94	C_{12} 3.10	C_{44} 0.34	B_T 0.51	KCl T = 850 K	C_{11} 6.04	C_{12} 2.85	C_{44} 7.00	B_T 6.97

It is interesting to note from Figures 1 to 4 that the values of C_{11} are decreasing with increase of temperature in all ionic solids. The values of C_{11} for MgO, CaO and NaCl are much better than previous theoretical results^{7-11,16-18} and very close to the experimental results².

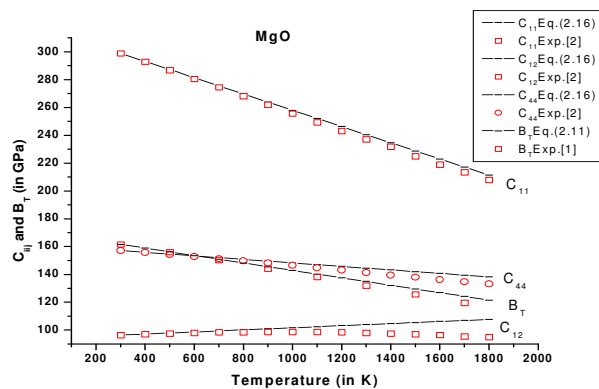


Fig.1. Temperature dependence of SOEC (C_{ij}) and bulk modulus (B_T) of MgO.

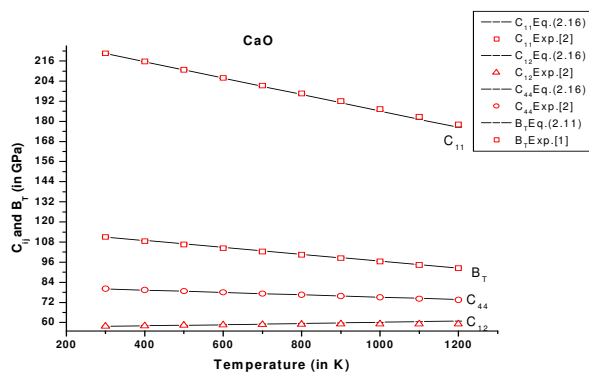


Fig.2. Temperature dependence of SOEC (C_{ij}) and bulk modulus (B_T) of CaO.

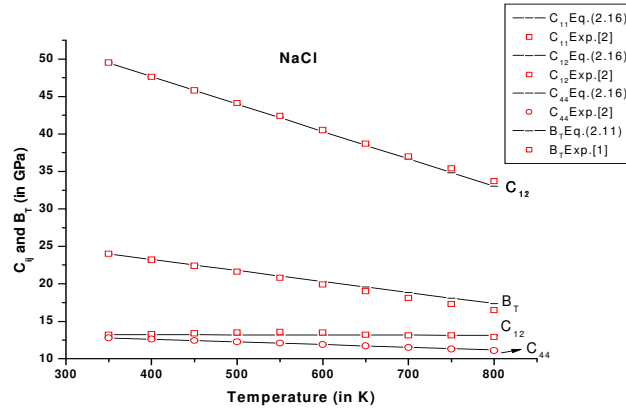


Fig.3. Temperature dependence of SOEC (C_{ij}) and bulk modulus (B_T) of NaCl.

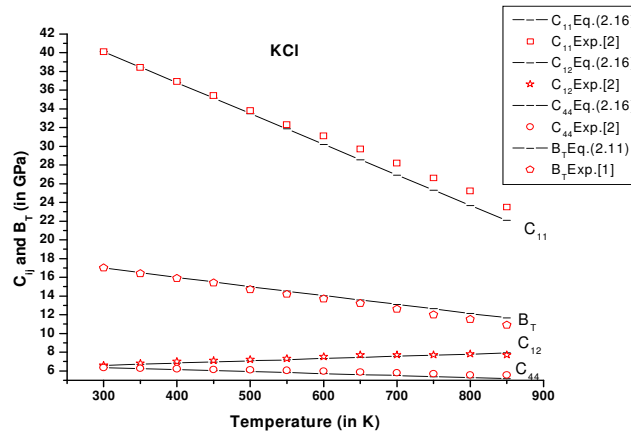


Fig.4. Temperature dependence of SOEC (C_{ij}) and bulk modulus (B_T) of KCl.

Similarly the computed the values of C_{12} are increasing slowly with increase of temperature in all cases and are good agreement with experimental data ² and much better than the earlier computed values ⁷⁻¹¹⁻¹⁶⁻¹⁷ in case CaO, NaCl and KCl except MgO. The computed values of C_{44} are close to the experimental values ² and are better than the earlier reported values ⁷⁻⁸⁻¹¹ in all cases. On the other hand the values of bulk modulus are in excellent agreement with the experimental values ¹ at different temperature and are better than the earlier study ¹¹⁻¹⁶⁻¹⁸.

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 ⁷⁻¹¹⁻¹⁶⁻¹⁸. It can be extended to

more complex solids like minerals of geophysical importance and applications.

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