

EFFECT OF TEMPERATURE ON VOLUME THERMAL EXPANSION OF MINERALS

Mahipal Singh*

Madan Singh**

ABSTRACT

The present study is based on the volume thermal expansion of some minerals under the effect of temperature. The volume thermal expansion (V/V_0) has been calculated using newly established integral form of equation of state (IFEOS) as proposed by Singh and Singh. This equation of state (EOS) has been applied to some minerals like NaCl, KCl, MgO, CaO, MnO, Fe_2SiO_4 , $MgAl_2O_4$, Olivine, Al_2O_3 and Mg_2SiO_4 . The results of volume thermal expansion (V/V_0) for these minerals have been compared with available experimental data as well as other theoretical results. A close agreement between theory and available experimental data supports the validity of Singh and Singh integral form of equation of state for minerals.

Keywords: Equation of state, Volume thermal expansion, Minerals, Temperature

PACS: 64.10.+h, 65.40.De, 66.70.-f

* Department of Physics, RH Govt. P. G. College, Kashipur, Uttarakhand, India-244713

** Department of Physics and Electronics, National University of Lesotho, Roma 180, Lesotho

1. Introduction

The behavior of minerals under extreme conditions of temperature and pressure plays an important role in understanding the dynamics and evolution of the lower mantle of the Earth. Due to the lack of direct samples from the lower mantle, seismic observations and laboratory measurements are the only available means to understand this region. Thus physical and chemical properties of minerals are crucial to understand the lower mantle of the Earth. The experimental data for the temperature dependence of thermodynamic quantities like thermal expansivity, isothermal bulk modulus, volume thermal expansion etc. for many materials has been compiled [1] which are considered to be most accurate.

The equation of state (EOS) plays a vital role in the study of the Earth deep interior. Using EOS, some important properties such as volume thermal expansion, bulk modulus, thermal expansivity etc. of candidate at lower mantle can be calculated. The studies based on the EOS at high temperature are of fundamental interest because they permit interpolation and extrapolation in to the regions in which the experimental data are not available adequately. Some researchers have evaluated various thermo elastic properties of minerals using various equations of state. A integral form of equation of state for volume thermal expansion has been established by some researchers [2] and used to study the volume thermal expansion of various materials. The volume expansion and bulk modulus data due to Anderson have been extrapolated by modification of previously used relationships for NaCl, KCl, MgO and CaO [3]. The unified theory of isobaric equation of state (EOS) has been used to obtain the temperature dependence of volume thermal expansion of various minerals like Al_2O_3 , Mg_2SiO_4 , Olivine, MgAl_2O_4 , Fe_2SiO_4 , MnO, NaCl and KCl [4]. Temperature dependence of volume thermal expansion ratio for ionic solids NaCl, KCl, MgO and CaO has been estimated by developing new expression for volume expansion [5] and it has been found that the Stacey reciprocal K-primed EOS is consistent with the experimental data for bulk modulus and thermal pressure as it yields correct values for volume expansion at high temperatures [6] and the comparison of calculated values with experimental data has been presented in the case of NaCl, KCl, MgO, CaO, Al_2O_3 and Mg_2SiO_4 . The thermo elastic properties of materials at high temperatures, specifically the thermal expansivity, volume thermal expansion and the isothermal bulk modulus have been studied using the Anderson formula for thermal expansivity and the interatomic potential functions within the framework of the Born model [7]. In the same direction, a linear relationship between volume

thermal expansion and temperature has also been established for the study of volume expansion for various materials [8].

Thus, so many equations of state are available for volume thermal expansion for different class of solids. But these equations of state involve either various approximations along with heavy computational work or more input parameters. To study the effect of temperature on volume thermal expansion of minerals by these equations of state is not an easy task. We, therefore, planned to develop a new and simpler integral form of equation of state for the study of temperature dependence of volume thermal expansion of various materials. Thus, the objective of the present study is to establish a simpler and straightforward integral form of equation of state for the evaluation of volume thermal expansion at different temperatures for minerals.

2. Method of analysis

It has been assumed that under the effect of temperature, the product of thermal expansion coefficient (α) and bulk modulus (K) remains constant [9] i.e.

$$\alpha K = \text{constant} \quad (1)$$

Differentiating Eq.(1) with respect to volume V at constant pressure P , we get

$$\alpha \left(\frac{dK}{dV} \right)_P = - \left(\frac{d\alpha}{dV} \right)_P K \quad (2)$$

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

$$\left(\frac{dK}{dT} \right)_P = - \left(\frac{K}{\alpha} \right) \left(\frac{d\alpha}{dT} \right)_P \quad (3)$$

Anderson Gruneisen parameter (δ_T) which relates thermal and elastic property of materials is defined as [1]

$$\delta_T = - \frac{1}{\alpha K} \left(\frac{dK}{dT} \right)_P \quad (4)$$

Using Eq.(3), the above equation takes the form

$$\delta_T = \frac{1}{\alpha^2} \left(\frac{d\alpha}{dT} \right)_P \quad (5)$$

Now applying the mathematical definition of thermal expansivity (α)

$$\alpha = \frac{1}{V} \left(\frac{dV}{dT} \right)_P \quad (6)$$

From Eqs.(5) and (6), we get

$$\delta_T = \frac{V}{\alpha} \left(\frac{d\alpha}{dV} \right)_P \quad (7)$$

From Eqs.(2) and (7), we get

$$\left(\frac{dK}{dV}\right)_P = -\left(\frac{\delta_T K}{V}\right) \quad (8)$$

A linear relationship between bulk modulus (K) and temperature (T) has been reported in the following way [8]

$$K = K_0[1 - \alpha_0 \delta_T^0 (T - T_0)] \quad (9)$$

where K , K_0 , α_0 and δ_T^0 are isothermal bulk modulus at temperature T , bulk modulus at $T = T_0$ i.e. at room temperature (reference temperature), volume thermal expansion coefficient at room temperature and Anderson Gruneisen parameter at $T = T_0$.

Differentiating Eq.(9) with respect to T at constant P

$$\left(\frac{dK}{dT}\right)_P = -K_0 \alpha_0 \delta_T^0 \quad (10)$$

From Eqs.(8) and (10), we have

$$\begin{aligned} \frac{\delta_T K}{V} \frac{dV}{dT} &= K_0 \alpha_0 \delta_T^0 \\ \text{or } \frac{dV}{V} &= \frac{K_0 \alpha_0 \delta_T^0}{\delta_T K} dT \end{aligned} \quad (11)$$

Anderson Gruneisen parameter has been expressed as [10, 11]

$$\delta_T = \delta_T^0 [1 - \delta_T^0 \ln\{1 - \alpha_0 \delta_T^0 (T - T_0)\}] \quad (12)$$

Using Eqs.(9) and (12), Eq.(11) takes the form as

$$\frac{dV}{V} = \frac{\alpha_0}{[1 - \delta_T^0 \ln\{1 - \alpha_0 \delta_T^0 (T - T_0)\}][1 - \alpha_0 \delta_T^0 (T - T_0)]} dT \quad (13)$$

Integrating Eq.(8), we get:

$$\int_{V_0}^V \frac{dV}{V} = \int_{T_0}^T \frac{\alpha_0}{[1 - \delta_T^0 \ln\{1 - \alpha_0 \delta_T^0 (T - T_0)\}][1 - \alpha_0 \delta_T^0 (T - T_0)]} dT \quad (14)$$

On rearranging the terms, which yields:

$$\frac{V}{V_0} = \exp \int_{T_0}^T \frac{\alpha_0}{(1 - \delta_T^0 \ln X)X} dT \quad (15)$$

where $X = \{1 - \alpha_0 \delta_T^0 (T - T_0)\}$

The above Eq.(15) is newly established Integral Form of Equation of State (IFEOS) for volume thermal expansion for materials. Since this new form of equation of state (EOS) has been developed by the authors of this paper Mahipal Singh & Madan Singh, therefore this EOS would be known as Singh & Singh Equation of State for volume thermal expansion. The beauty of this equation of state is that it requires only two input parameters α_0 and δ_T^0 at room temperature

(reference temperature) and the value of V/V_0 is evaluated directly as a function of temperature. This equation is also easier to handle in comparison of already existing integral form of equation of state [2]. This newly developed EOS is independent of the crystal structure of the material under investigation. Therefore, it can expectedly be applied to study temperature dependent volume expansion of a wide variety of materials.

The following expression for temperature dependence of V/V_0 has been obtained as [8]

$$\frac{V}{V_0} = 1 - \frac{1}{\delta_T^0} \ln\{1 - \alpha_0 \delta_T^0 (T - T_0)\} \quad (16)$$

The values of volume thermal expansion (V/V_0) as a function of temperature (T) for different minerals NaCl, KCl, MgO, CaO, MnO, Fe_2SiO_4 , MgAl_2O_4 , Olivine, Al_2O_3 and Mg_2SiO_4 have been calculated by Eq.(15). The theoretical results obtained by Singh & Singh EOS have been compared with the results obtained by Eq.(16) and other existing experimental results.

3. Results and discussion

The values of volume thermal expansion (V/V_0) at different temperatures have been calculated using newly established Singh and Singh equation of state for volume thermal expansion Eq.(15) and also using Eq.(16) for NaCl, KCl, MgO, CaO, MnO, Fe_2SiO_4 , MgAl_2O_4 , Olivine, Al_2O_3 and Mg_2SiO_4 minerals. These equations need only two input parameters i.e. Anderson Gruneisen parameter (δ_T^0) and volume thermal expansion coefficient (α_0) at room temperature (reference temperature). The input parameters used in this theoretical work are given in Table 1.

Table 1 : Input parameters used in the present work [1]

Mineral	α_0 (10^{-5} K^{-1})	δ_T^0
NaCl	11.8	5.56
KCl	11	5.84
MgO	3.12	5.26
CaO	3.04	6.19
MnO	3.46	5.96
Fe_2SiO_4	2.61	7.34
MgAl_2O_4	2.11	7.73
Olivine	2.66	6.59

Al_2O_3	2.14	5.70
Mg_2SiO_4	2.72	5.94

The calculated values of volume thermal expansion (V/V_0) with temperatures (T) for NaCl, KCl, MgO, CaO, MnO, Fe_2SiO_4 , MgAl_2O_4 , Olivine, Al_2O_3 and Mg_2SiO_4 minerals using IFEOS Eq.(15) are plotted in Figs. 1-10 and compared with theoretical [8] and experimental data [1] for the sake of comparison of our theoretical results. It is obvious from Figs. 1-10 that relative volume thermal expansion (V/V_0) increases with increase in temperature. The inter-atomic separation increases on increasing the temperature of the solid and hence there is thermal expansion in solids. Due to thermal expansion, the anharmonicity of the lattice vibrations are produced. It is also obvious that our calculated theoretical results of volume thermal expansion (V/V_0) for all the minerals under study are in close agreement with the existing experimental [1] and theoretical results [8]. Thus it is emphasized here that our integral form of equation of state Eq.(15) successfully explains the volume thermal expansion of all minerals under study which in turn reveals the validity of the present work.

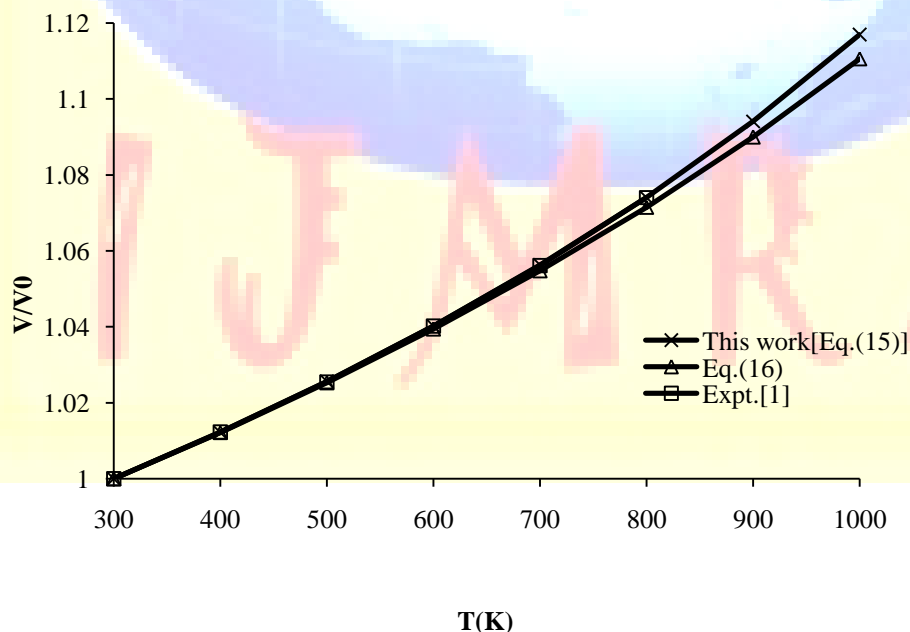


Fig.1: Variation of volume thermal expansion (V/V_0) with temperature (T) for NaCl

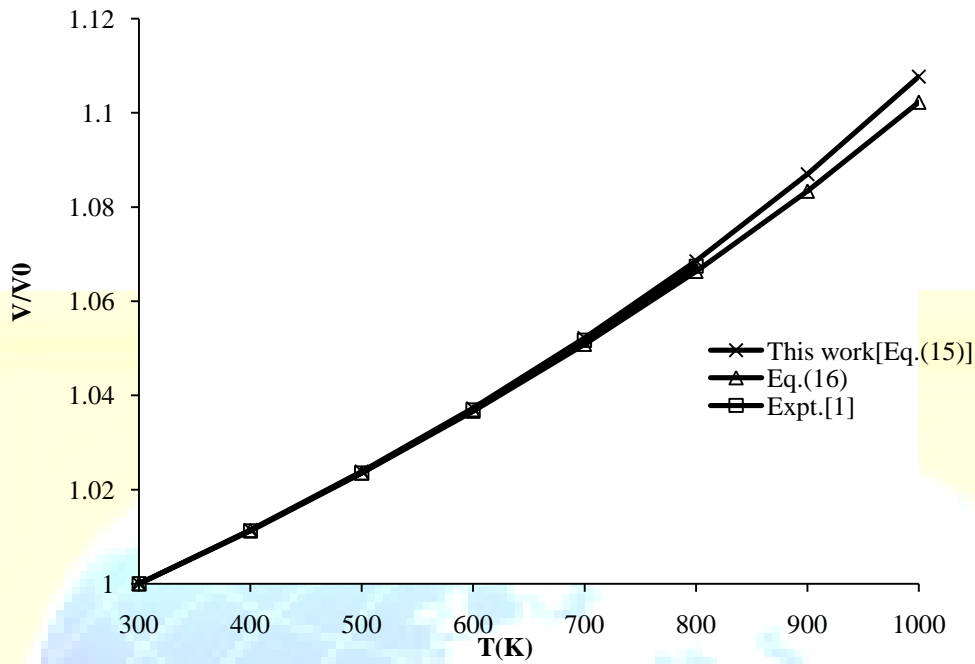


Fig.2: Variation of volume thermal expansion (V/V_0) with temperature (T) for KCl

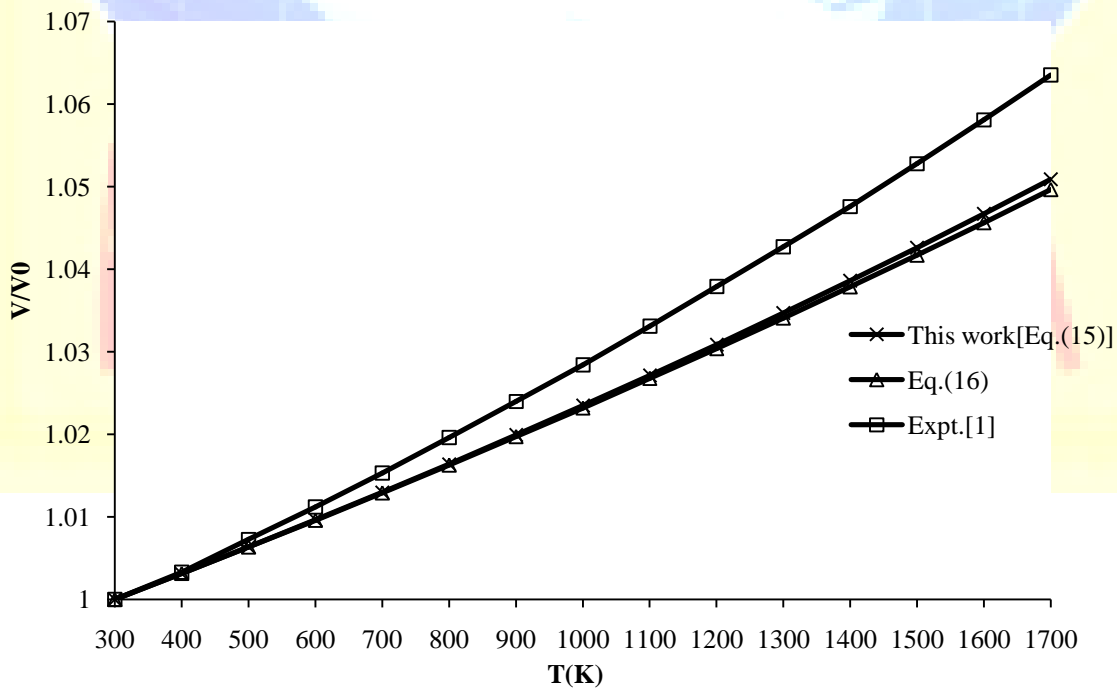


Fig.3: Variation of volume thermal expansion (V/V_0) with temperature (T) for MgO

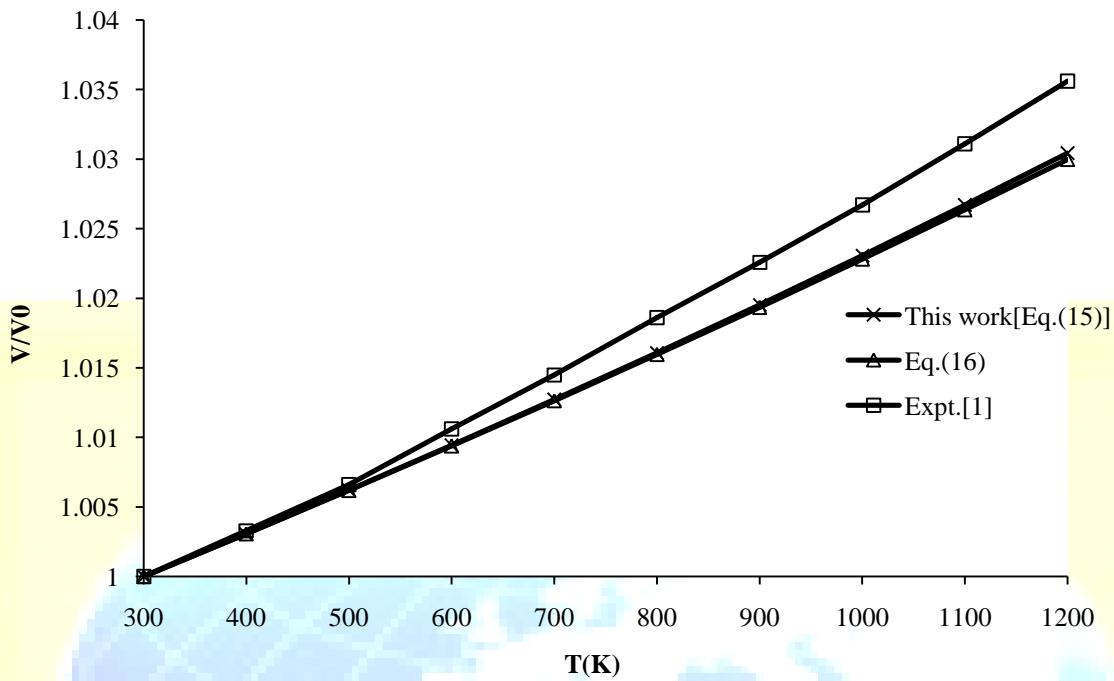


Fig.4: Variation of volume thermal expansion (V/V_0) with temperature (T) for CaO

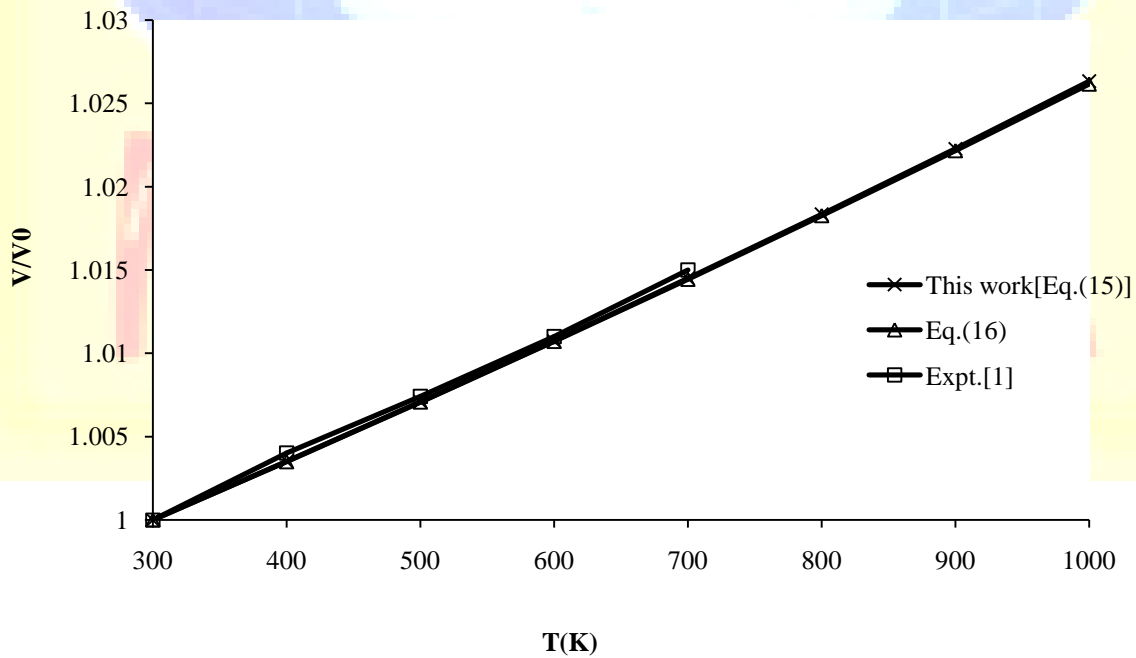


Fig.5: Variation of volume thermal expansion (V/V_0) with temperature (T) for MnO

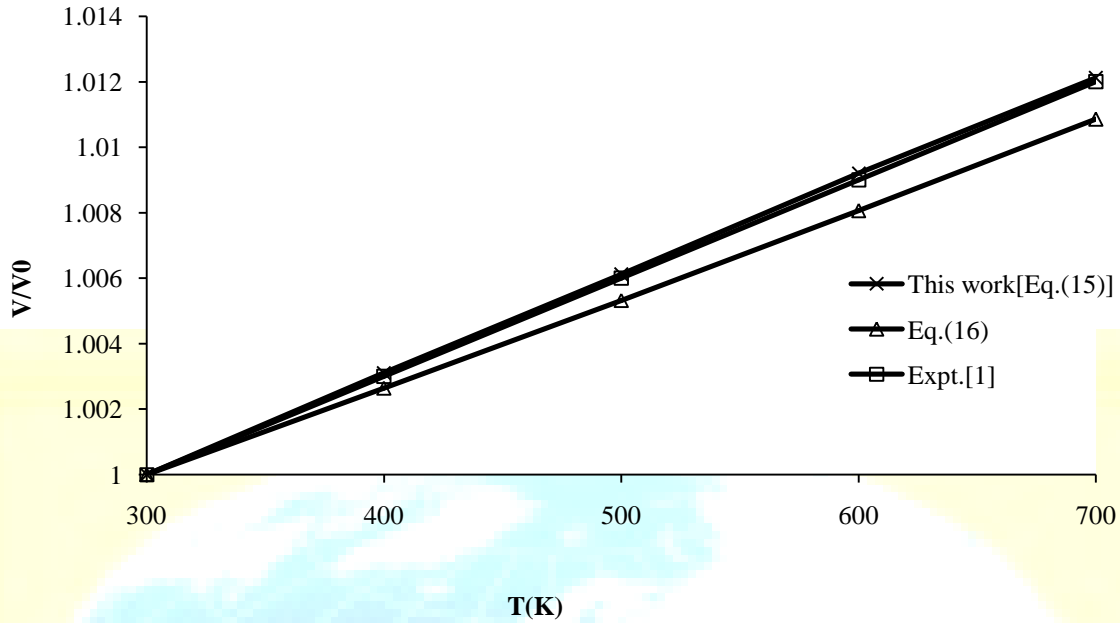


Fig.6: Variation of volume thermal expansion (V/V_0) with temperature (T) for Fe_2SiO_4

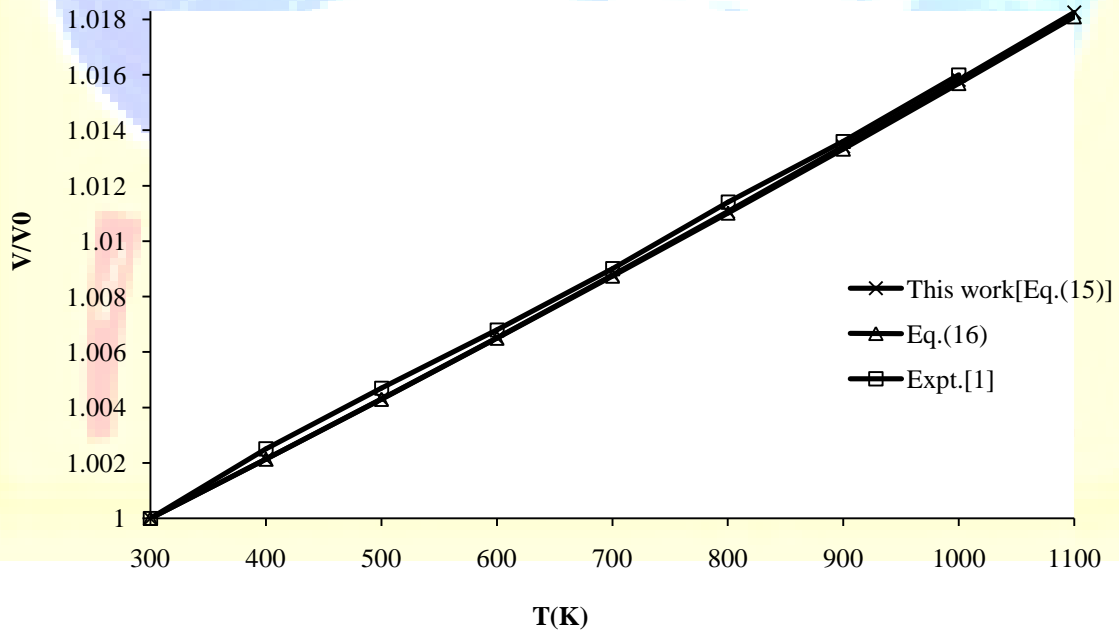


Fig.7: Variation of volume thermal expansion (V/V_0) with temperature (T) for $MgAl_2O_4$

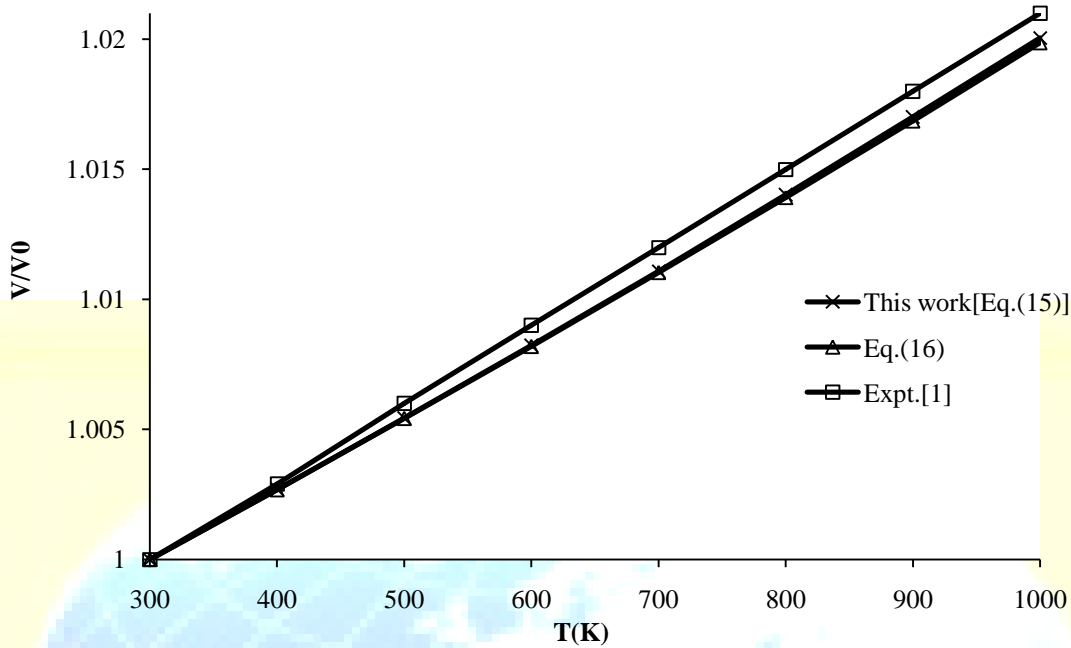


Fig.8: Variation of volume thermal expansion (V/V_0) with temperature (T) for Olivine

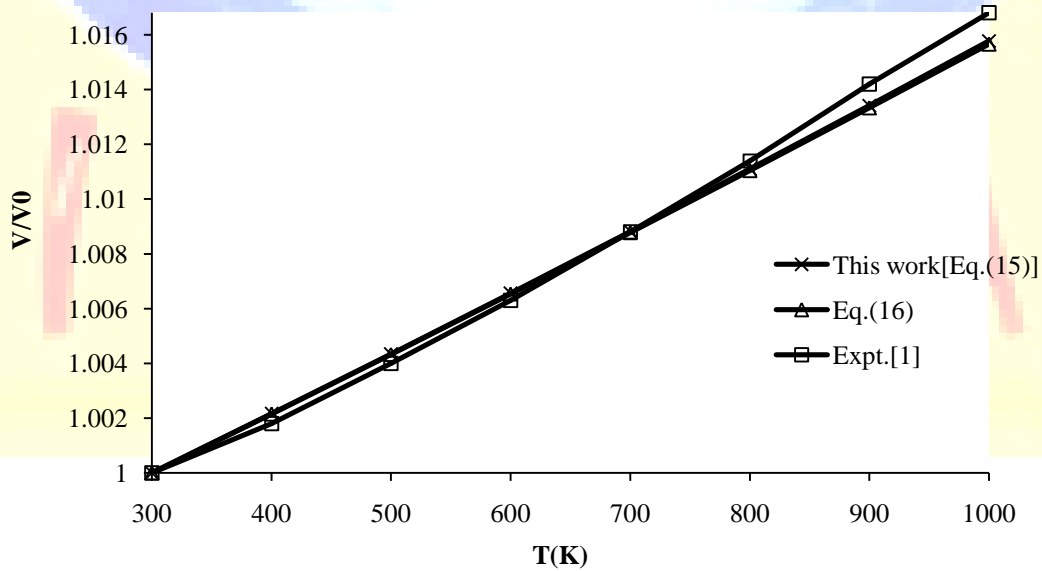


Fig.9: Variation of volume thermal expansion (V/V_0) with temperature (T) for Al_2O_3

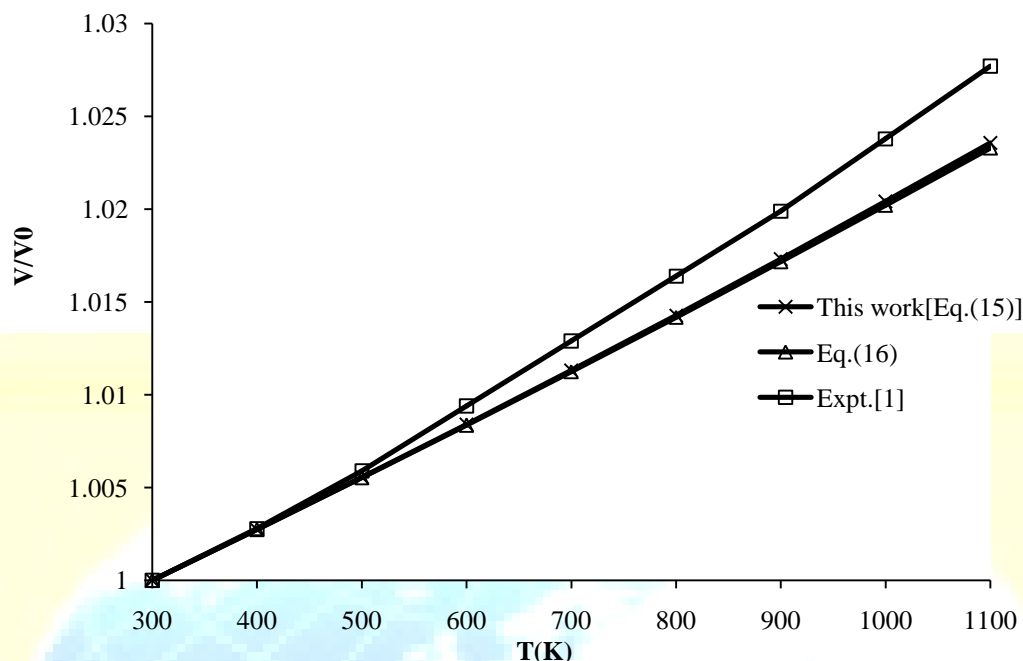


Fig.10: Variation of volume thermal expansion (V/V_0) with temperature (T) for Mg_2SiO_4

4. Conclusion

In the present work, a new integral form of equation of state (IFEOS) for volume thermal expansion has been established which is named as Singh and Singh equation of state. The values of volume thermal expansion (V/V_0) at different temperatures for a wide variety of minerals NaCl, KCl, MgO, CaO, MnO, Fe_2SiO_4 , $MgAl_2O_4$, Olivine, Al_2O_3 and Mg_2SiO_4 have been calculated using this newly established Singh and Singh EOS. Our calculated theoretical results on volume thermal expansion (V/V_0) are found to be in close agreement with the existing experimental [1] and theoretical results [8]. It is emphasized here that our IFEOS (Singh and Singh EOS) successfully explains the volume thermal expansion of minerals under study which in turn reveals the validity of the present work.

References

- [1] O.L. Anderson, Equation of State for Geophysics and Ceramic Sciences, Oxford University Press, Oxford, 1995.
- [2] K.Y. Singh, B.R.K. Gupta, Physica B 334 (2003) 266.
- [3] S.K. Srivastava, P. Sinha, M. Panwar, Indian J. of Pure & Applied Physics 47 (2009) 175.
- [4] G. Nand, M. Kumar, Indian J. of Pure & Applied Physics 47 (2009) 867.
- [5] S.K. Srivastava, P. Sinha, Indian J. of Pure & Applied Physics 49 (2011) 195.
- [6] S.S. Kushwah, Y.S. Tomar, Indian J. of Pure & Applied Physics 49 (2011) 99.
- [7] K. Sunil, B.S. Sharma, Indian J. of Pure & Applied Physics 50 (2012) 387.
- [8] Z.H. Fang, Physica B 357 (2005) 433.
- [9] O.L. Anderson, K. Zou, Phys. Chem. Miner. 16 (1989) 642.
- [10] N. Chuanhui, S. Huang, W. Huang, Applied Physics Research 2(1) (2010) 144.
- [11] M. Singh, International J. of Phys. & Research 3(4) (2013) 55.