ABSTRACT

Various isothermal Equations of State (EoS) are used to study the pressure-volume relationships and the isothermal bulk modulus ($K_T$) of geophysical minerals. The study of Anderson-Grüneisen parameter ($\delta_T$) not only provides information about interatomic forces but also predict the microscopic behaviour of different thermodynamic properties. At high temperatures the extrapolation of thermal expansivity ($\alpha$) is done on the basis of its non-linear model with change in temperature. Non-linear relationships for thermal expansivity ($\alpha$) and isothermal bulk modulus ($K_T$) are the results of anharmonic effects in high temperature region, i.e. at temperature greater than Debye temperature. At very high compression the thermal expansivity ($\alpha$) is almost independent of temperature. The product of thermal expansivity and isothermal bulk modulus remains constant in high temperature region but such approximation does not hold well. The Anderson-Grüneisen parameter is also useful for solving certain geophysical and astrophysical problems. Thermal expansivity is very important parameter to interpret the thermodynamic and thermo elastic behaviour of materials at high temperature and pressure because most of the errors in calculations of thermodynamic functions arise due to the uncertainty of thermal expansivity at high temperatures and pressures.

In present study three K-prime EoSs by studying the pressure-volume (P-V) relation, the isothermal bulk modulus ($K$) and first pressure derivative ($K'$) for geo physical minerals such as MgO, Mg$_2$SiO$_4$, MgSiO$_3$, Al$_2$O$_3$ and CaO at selected temperatures ranging from room temperature up to their melting point under high compressions down to $V/V_0 = 0.60$, where $V_0$ is the volume $V$ at $P = 0$, have been utilized. The values of $P$, $K$ and $K'$ were calculated through three EoSs, which are generally found same throughout the compression range for all the geophysical minerals. The first pressure derivate of bulk modulus ($K'$), is a very important parameter to develop various equations of state (EoS). Similar results were obtained from Keane, Stacey and Sinha Equations of State. The pressure and isothermal bulk modulus ($K$) increases as with the increase in compression. However, these parameters decrease with the increasing temperature for all the geophysical minerals. The values of $K'$ decrease as the compression increases, however, it increases with the increase in temperature for all the geophysical minerals under study. The results obtained in the present study are in agreement with available experimental P-V-T data for MgO and MgSiO$_3$. An EoS provides pressure-volume–
temperature (P-V-T) relationships for solids and helps for predicting a variety of properties under different conditions of pressure, volume and temperature.

The analysis of the temperature dependence of thermal pressure for $\text{Mg}_2\text{SiO}_4$, $\text{MgAl}_2\text{O}_4$, $\text{MnO}$, $\text{Fe}_2\text{SiO}_4$, $\text{NaCl}$ and $\text{KCl}$ revealed that thermal pressure is an important physical quantity playing a vital role in the evolution of high temperature Equation of States for solids. Various models for the determination of the temperature dependence of thermal pressure ($P_{th}$) were critically examined in the light of experimental data. The temperature dependence of thermal pressure for $\text{Mg}_2\text{SiO}_4$, $\text{MgAl}_2\text{O}_4$, $\text{MnO}$, $\text{Fe}_2\text{SiO}_4$, $\text{NaCl}$ and $\text{KCl}$ geophysical minerals was computed through Keane EoS. The computed values were also compared with available experimental data. A relationship to predict temperature dependence of elastic constants and thermal energy for geophysical minerals was established by using a formulation for volume dependence isothermal Anderson- Grüneisen parameter which is valid up to extreme compression limit $P \rightarrow \infty$ or $V \rightarrow 0$ on geophysical minerals viz. $\text{MgO}$, $\text{CaO}$, $\text{Mg}_2\text{SiO}_4$ and $\text{Al}_2\text{O}_3$. The values of isothermal bulk modulus ($K_T$) and adiabatic bulk modulus ($K_S$) for geophysical minerals viz. $\text{MgO}$, $\text{CaO}$, $\text{Mg}_2\text{SiO}_4$ and $\text{Al}_2\text{O}_3$ at $P = 0$ were determined and compared with available experimental values. The plots between thermal energy ($E_{th}$) and isothermal bulk modulus exhibit linearity for ionic solids, which is attributed to the linear relation of thermal pressure and isothermal pressure at high temperatures. The thermal energy shows the linearity with thermal pressure. Subsequently the thermal energy shows the linearity with the isothermal bulk modulus ($K_T$). This concept was extended to other elastic properties $K_S$, $C_{11}$, $C_{44}$ and $C_s$ for geophysical minerals under study. The thermal energy also shows linearity with adiabatic bulk modulus ($K_S$), and elastic constants viz. $C_{11}$, $C_{33}$, $C_{44}$ and $C_s$ for the geophysical minerals under study. The results show the reliability with the generalized data based on the $K_T$, $K_S$, $C_{11}$, $C_{33}$, $C_{44}$ and $C_s$ with the experimental data. Also, $E_{th}$ versus $T$ plot shows linear nature and the thermal energy shows linearity with elastic moduli such as $K_T$, $K_S$, $C_{11}$, $C_{33}$, $C_{44}$ and $C_s$ for geophysical minerals under study.

A model was introduced to predict the values of thermal expansivity for geophysical minerals such as $\text{MgO}$, $\text{Al}_2\text{O}_3$, and $\text{Mg}_2\text{SiO}_4$. Thermal expansivity is a necessary parameter for solving many problems of material science and geophysics and many thermal and elastic properties can also be derived from it. The volume expansion of
solids due to the rise in temperature is directly related to thermal pressure. The Equation of State (EoS) is effectively important in studying the properties of solids under high pressure and high temperature. The value of thermal expansivity (α) is predicted by the use of isothermal bulk modulus (KT) and thermal pressure (Pth). A close agreement was found for all geophysical minerals used in the present study and shows the validity of present model.

Moreover, a simple and straightforward empirical relationship of volume dependence of Grüneisen ratio was evolved. Grüneisen ratio is a very important parameter used to quantify the relationship between thermal and elastic properties of solids. The Grüneisen ratio can be considered as a measure of the change of pressure resulting from the increased energy density at constant volume. Grüneisen ratio is also useful to investigate the anharmonic property of materials. It is known that Mg2SiO4 is an important material as well as geophysical mineral. It is one of the few materials for which sufficient data is available. There is a wide range of stability in temperature-pressure space and it is regarded as a major component of the Earth lower mantle which makes Mg2SiO4 attractive for the study. A simple method to investigate the volume dependence of the Grüneisen ratio at high temperatures of Mg2SiO4 down to a range of volume ratio 0.90 was adopted. The volume dependence of the Grüneisen ratio for Mg2SiO4 was also studied. The results obtained through it are comparable. An expression to estimate the values of volume dependence of thermal expansivity was developed. The present study has been employed on the geophysical minerals viz. MgO, Al2O3 and Mg2SiO4. For these minerals, the thermal expansivity decreases with the decrease in volume ratio or with the increase in compression. However, it increases with the increasing temperatures.

The thesis comprises of following chapters:

**Chapter 1** - includes introduction to geophysical minerals of the Earth’s lower mantle and core. Pressure-Volume-Temperature (P-V-T) relationships for solids such as MgO, CaO, Al2O3 and Mg2SiO4 under different conditions of pressure, volume and temperature. This chapter also includes critical review of the available literature on geophysical minerals.
Chapter 2 - explores the various Equations of State (EoS) like Keane EoS, Stacey EoS and Sinha EoS.

Chapter 3 - describes the thermal and elastic properties of solids i.e. thermal expansivity, thermal pressure, isothermal bulk modulus and elastic constants.

Chapter 4 - explains Grüneisen ratio and Anderson-Grüneisen parameter. Higher order derivative of Grüneisen parameter and anharmonicity of Grüneisen parameter.

Chapter 5 - includes P-V-T relationships for geophysical minerals, volume thermal expansion for solids such as Mg$_2$SiO$_4$, MgAl$_2$O$_4$, MnO, Fe$_2$SiO$_4$, NaCl and KCl, thermal expansivity for MgO, Al$_2$O$_3$ and Mg$_2$SiO$_4$, volume dependence of Grüneisen parameter for Mg$_2$SiO$_4$, elastic constants at high temperatures for MgO, CaO, Mg$_2$SiO$_4$ and Al$_2$O$_3$ and volume dependence of thermal expansivity for MgO, Al$_2$O$_3$ and Mg$_2$SiO$_4$.

Conclusions - present a brief of the outcomes of the present investigations.