IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)

An International Open Access, Peer-reviewed, Refereed Journal

Analysis Of Pressure-Volume-Temperature Relationships For Alkaline Earth Oxides Mgo And Cao

K. Sunil[1*], S. Rekha[1], S. Pushpendra[1], P. K. Singh[2]

[1]Department of Physics, Institute of Engineering and Technology, Swami Vivekanand Campus Khandari, Dr Bhimrao Ambedkar University, Agra 282002- India

[2]Department of Physics, Shri Sadguru Saibaba Science and Commerce College , Ashti, Gadchiroli 442707- India

Abstract

The pressure-volume-temperature relationships of a material can be investigated using an equation of state (EOS). In the present study we make use of the Holzapfel adapted polynomial of second order (AP2) EOS for determining pressure-volume relationships along selected isotherms, volume-temperature relationships along different isobars, and pressure-temperature relationships along selected isochores for MgO and CaO. The results have been discussed and found to provide new insight for understanding thermodynamics of solids.

Keywords : MgO; CaO; Holzapfel equation of state; Thermal pressure; Thermodynamic properties.

1. Introduction

There are four basic thermodynamic variables viz. pressure P, volume V, temperature T and entropy S which describe thermodynamic behaviour of materials [1, 2]. The variation of volume V with pressure along an isotherm gives isothermal compressibility which is iverse of bulk modulus. The variation of volume with temperature along an isobar yields thermal expansivity also known as isobaric volume thermal expansion coefficient α. Thus we have

$$K_T = -V\left(\frac{dP}{dV}\right)_T \qquad (1)$$

and

$$\alpha = \frac{1}{V}\left(\frac{dV}{dT}\right)_P \qquad (2)$$

The variation of pressure with temperature along an isochore can be written as follows

$$\left(\frac{dP}{dT}\right)_V = \alpha K_T \qquad (3)$$

Equation (3) on integration yields the following expression for thermal pressure

$$P_{th} = \int_{T_0}^{T} \alpha K_T dT \qquad (4)$$

When a material is heated to increase its temperature from T_0 to T so that the volume is increased from V_0 to V. Thermal pressure is then defined as the pressure required to compress the solid from V to V_0 [3]. The relationship between pressure P and volume V can be investigated using an equation of state (EOS). It has been found [4-7] that the Holzapfel adapted polynomial of second order (AP2) EOS yields quite accurate results for the entire range of volume compression. In the present study we make use of the Holzapfel EOS for investigating the thermodynamic behaviour of MgO and CaO.

2. Method of Analysis

The Holzapfel AP2 EOS can be written as follows [8, 9]

$$P = 3K_0 x^{-5}(1-x)[1+C_2 x(1-x)]\exp C_0(1-x) \tag{5}$$

where $x = (V/V_0)^{1/3}$, V is the volume at pressure P, and V_0 at zero-pressure. K_0 is the value of bulk modulus K at P=0, and

$$C_0 = -\ln\left(\frac{3K_0}{P_{FGO}}\right) \tag{6}$$

where the Fermi gas pressure is

$$P_{FGO} = a_{FG}\left(\frac{Z}{V_0}\right)^{5/3} \tag{7}$$

The constant C_2 in Eq. (5) is given below

$$C_2 = \frac{3}{2}(K_0' - 3) - C_0 \tag{8}$$

Here K_0' is the pressure derivative of bulk modulus K' = dK/dP at zero-pressure. Equation (5) gives a correct Thomas-Fermi limit of pressure at extreme compression. P_{FGO} is the pressure of Fermi gas with a_{FG} = 0.02337 GPa $(nm)^5$, z is the total number of electrons per molecule multiplied by the Avogadro number. V_0 is the volume in cm^3/mol. The EOS parameters used in computations are given in Table 1.

The EOS represented by Eq. (5) is applicable at initial temperature T_0 equal to 300 K, the room temperature. At elevated temperatures $T > T_0$, we have to modify Eq. (5) by incorporating temperature effects in terms of thermal pressure as follows [1, 3]

$$P(V,T) = P(V,T_0) + \Delta P_{th} \tag{9}$$

where $P(V, T_0)$ is given by Eq. (5), and ΔP_{th} can be determined by using Eq. (4) as follows

$$\Delta P_{th} = \alpha K_T (T - T_0) \tag{10}$$

Eq. (10) has been derived from Eq. (4) by assuming that the product αK_T remains constant with the change in temperature.

3. Results and Discussion

Equations (5), (9) and (10) have been used in computations to obtain pressure-volume relationships along selected isotherms and volume-temperature relationships along selected isobars. The results have been determined for MgO upto about 200 GPa, and for CaO upto 60 GPa. MgO and CaO remains stable in NaCl (B_1) strcuture up to these pressures [10, 11]. The results are plotted in Figures 1-4. It should be mentioned that the thermal pressure increases with the increase in temperature. The required pressure therefore increases with the increase in temperature for a given value of volume compression (V/V_0) as shown in Figures 1 and 2. The results are compared with the available experimental data [14-16].

The variations of volume with temperature along different isobars are plotted in Figures 3 and 4 for MgO and CaO respectively. It is found that the rate of variation of volume with temperature is maximum along P = 0. As the value of pressure increases the rate of V with T becomes smaller and smaller. This is mainly because the thermal expansivity decreases with the increase in pressure due to the fact that anharmonicity of crystals is suppressed at high pressures [17, 18].

Acknowledgements

Thanks are due to Dr. Jai Shanker for some very useful discussions.

References

[1] O.L. Anderson, Equation state of solids in geophysics and ceramic science, Oxford University Press Inc. New York 1995.

[2] F.D. Stacey, High pressure equations of state and planetary interiors, Rep. Prog. Phys. **68**, 341 (2005).
https://doi.org/10.1088/0034-4885/68/2/R03

[3] J. Shanker, S.S. Kushwah, P. Kumar, Theory of thermal expansivity and bulk modulus for MgO and other minerals at high temperatures. Physica B. **233**, 78 (1997).
https://doi.org/10.1016/S0921-4526(96)01238-0

[4] A.B., Belonoshko, E.I. Isaev, N.V. Skorodumova, B. Johansson, Stability of the body-centered tetrogonal phase of Fe at high pressure : Ground-state energies, phonon spectra, and molecular dynamics simulations, Phys. Rev. B. **74**, 214102 (2006).
https://doi.org/10.1103/PhysRevB.74.214102

[5] P.K. Singh, Analysis of pressure-volume-temperature relationship for $MgSiO_3$ perovskite, High Temp.-High Press. **47**, 269 (2018).

[6] P.K. Singh, Equation of state and thermoelastic properties of Mg_2SiO_4, Comp. Cond. Matter. **31**, e00678 (2022).
https://doi.org/10.1016/j.cocom.2022.e00678

[7] K. Sunil, P.K. Singh, K. Dharmendra, Prediction of melting curves of ionic and partially covalent compounds using the Jeanloz equation for the Grüneisen parameter. Appl. Phys. A. **467**, 1 (2024).
https://doi.org/10.1007/s00339-024-07599-0

[8] W.B. Holzapfel, Physics of solids under strong compression Rep. Prog. Phys. **59**, 29 (1996).
http://dx.doi.org/10.1088/0034-4885/59/1/002

[9] W.B. Holzapfel, Equations of state for solids under strong compression, High Press. Res. **16**, 81 (1998).
https://doi.org/10.1080/08957959808200283

[10] J.K. Wicks, S. Singh, M. Millot, D.E. Fratanduona et al., B_1-B_2 transition in shock-compressed MgO, Sci. Adv. **10**, 1 (2024).
https://doi.org/10.1126/sciadv.adk0306

[11] R. Jeanloz, T.J. Ahrens, H.K. Mao, P.M. Bell, B_1-B_2 transition in calcium oxide from shock-wave and diamond-cell experiments, Science **206**, 829 (1979).
https://doi.org/10.1126/science.206.4420.829

[12] P. Gupta, Analysis of melting of geophysical minerals at high pressures based as the generalized Rydberg EOS. J. Alloys Compd. **475**, 479 (2009).
https://doi.org/10.1016/j.jallcom.2008.07.075

[13] J. Shanker, M.P. Sharma, S.S. Kushwah, Analysis of melting of ionic solids based on the thermal equation of state, J. Phys. Chem. Solids. **60**, 603 (1999).
https://doi.org/10.1016/S0022-3697(98)00323-0

[14] Z. Wang, B. Schott, P. Lazor, S.K. Saxena, Improved equations for addressing the high pressure melting of metastable silicate perovskites. J. Alloys Compd. **315**, 51 (2001).
https://doi.org/10.1016/S0925-8388(00)01310-4

[15] O.L. Anderson, D.G. Isaak, H. Oda, Thermoelastic parameters for six minerals at high temperature, J. Geophys. Res. **96**, 18037 (1991).
https://doi.org/10.1029/91JB01579

[16] I. Suzuki, Thermal expansion of periclase and olivine, and their anharmonic properties, J. Phys. Earth. **23**, 145 (1975).
https://doi.org/10.4294/jpe1952.23.145

[17] B.B. Karki, First-principles determination of elastic properties of $CaSiO_3$ perovskite at lower mantle pressure. Geophys. Res. Letters. **25**, 2741 (1998).
https://doi.org/10.1029/98GL51952

[18] B.B. Karki, Thermal pressure in MgO and $MgSiO_3$ perovskite at lower mantle conditions. Am. Min. **85**, 1447 (2000).
https://doi.org/10.2138/am-2000-1013

Table 1 : Values of EOS parameters for MgO and CaO [1, 3, 12-14].

	V_0 (cm^3/mol)	K_0 (GPa)	K'_0	C_0	C_2	αK_T ($10^{-3}K^{-1}$ GPa)
MgO	11.25	162	4.15	1.684	0.041	5.67
CaO	16.75	111	4.85	1.959	0.816	3.72

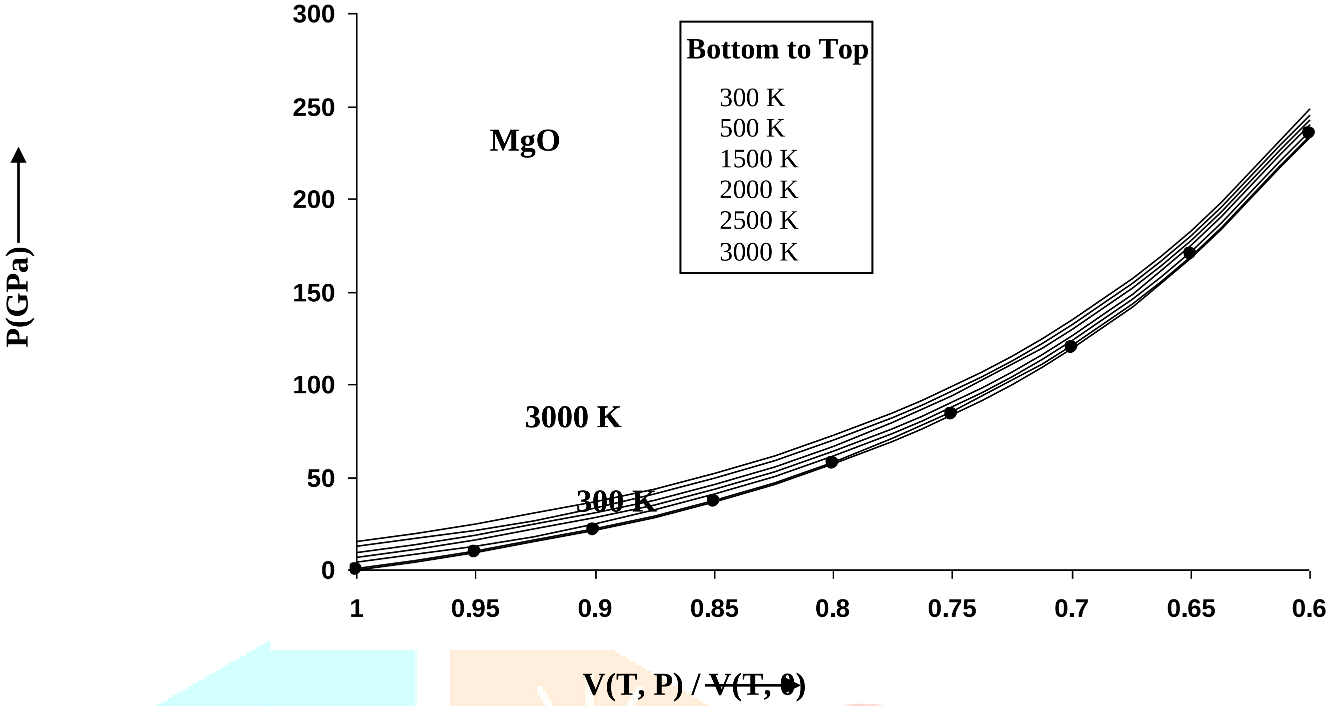

Figure 1 : Variations of pressure P(GPa) with V(T, P) / V(T, 0) for MgO determined from the Holzapfel AP2 EOS, and thermal pressures. Experimental data are represented by symbol (●) [1].

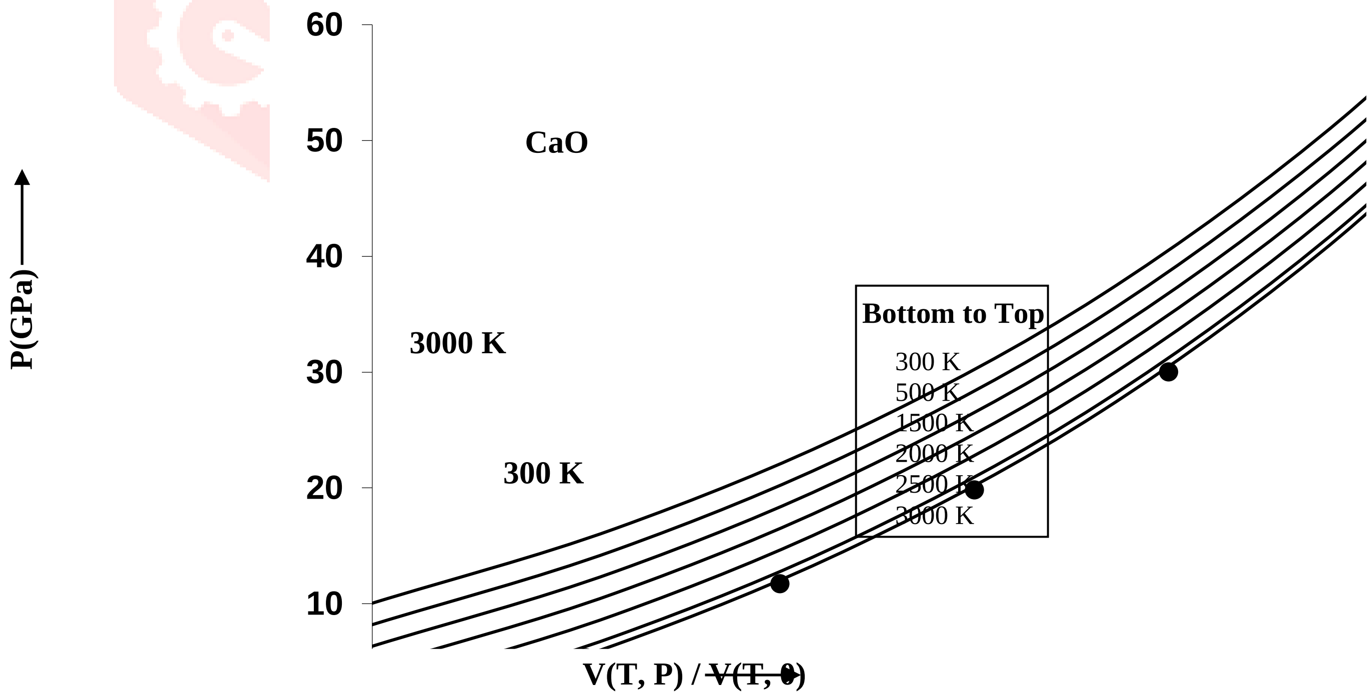

Figure 2 : Variations of pressure P(GPa) with V(T, P) / V(T, 0) for CaO determined from the Holzapfel AP2 EOS, and thermal pressures. Experimental data are represented by symbol (●) [1].

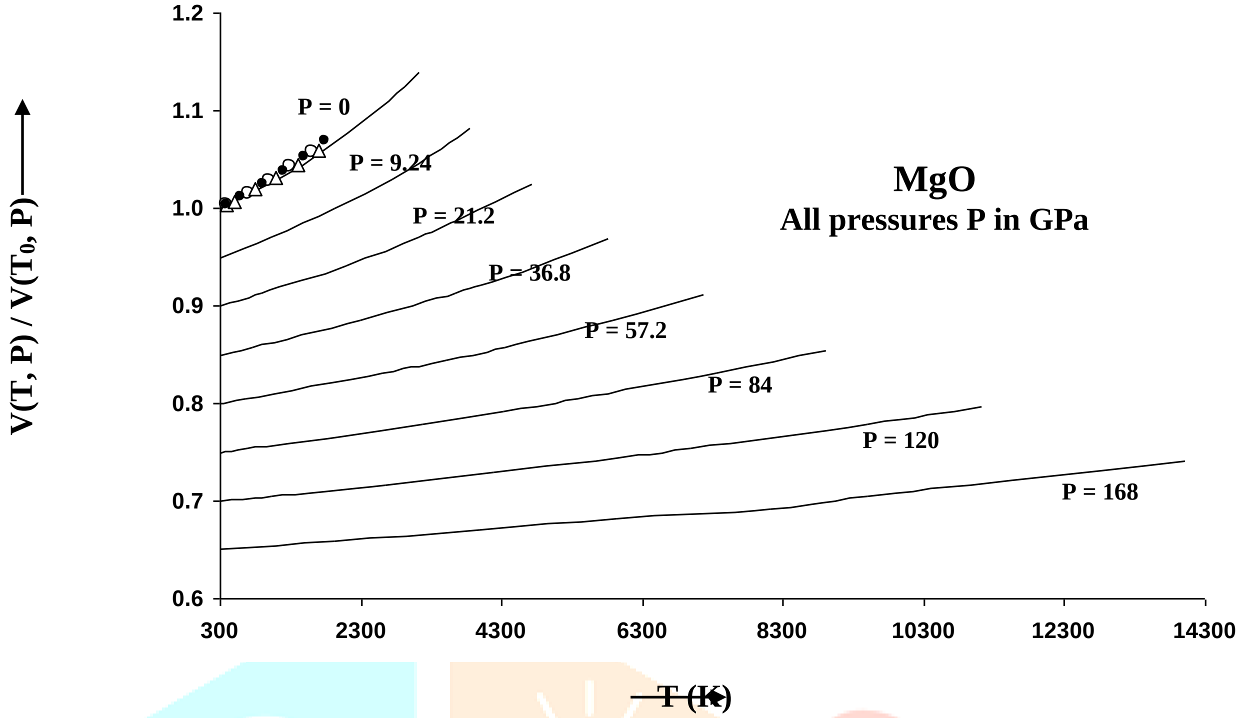

Figure 3 : Plots between V(T, P) / V(T_0, P) and T(K) for MgO along different isobars at selected pressures determined from Eq. (9). Experimental data are represented by symbol (●) [15] and results obtained by Suzuki et al [16] and Shanker et al. [3] are given by symbols (▲), (○) respectively.

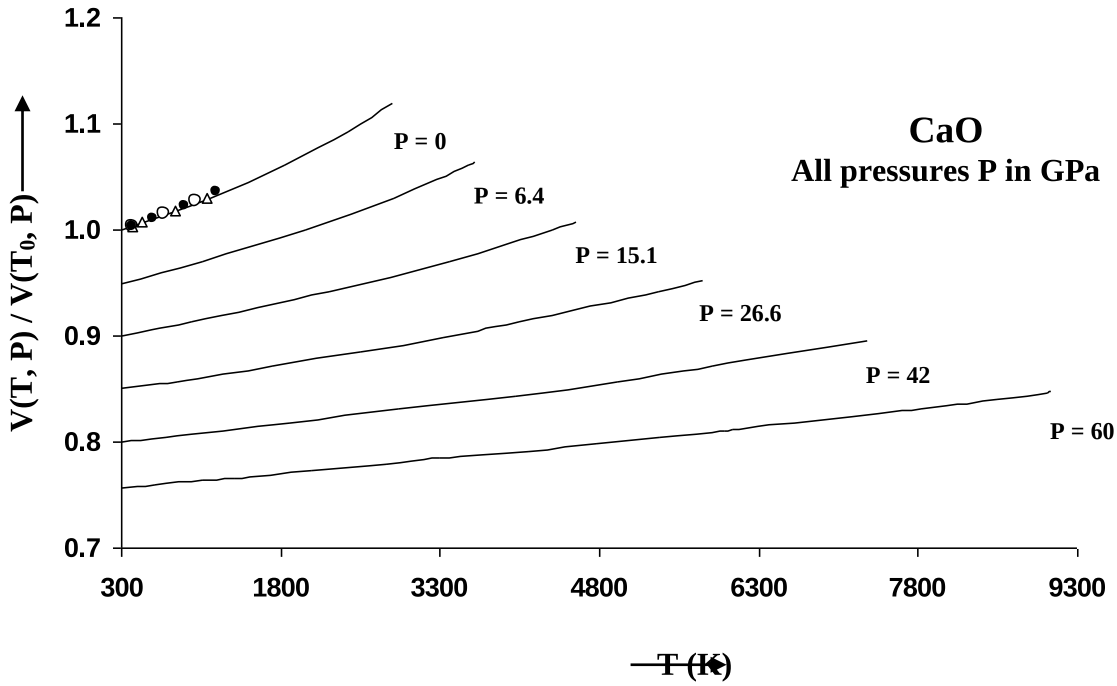

Figure 4 : Plots between V(T, P) / V(T_0, P) and T(K) for CaO along different isobars at selected pressures determined from Eq. (9) Experimental data are represented by symbol (●) [15]. The results obtained by Suzuki et al [16] and Shanker et al. [3] are given by symbols (▲), (○) respectively.