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ANALYSIS OF THERMOELASTIC PROPERTIES OF SOME GEOPHYSICAL MINERALS AT HIGH PRESSURES

Dharmendra Singh and Dr. Amita
Research Scholar,
Department of Physics, R.B.S. College, Agra
Dr. Bhimrao Ambedkar University, Agra-282002 (U.P.) India

Abstract

We have investigated equation of state and thermoelastic properties of some geophysical minerals viz. MgO, CaO BaO and Fe_2SiO_4. Presure-volume relationship, bulk modulus and its pressure derivative have been calculated using the Birch-Murnaghan third order equation of state (EOS) and the Vinet-Rydberg EOS. The results for the solids under study determined from the two EOSs have been compared with the available experimental data. The Grüneisen parameter as a function of volume has been determined using the generalized free volume formula. The volume dependence of free volume parameter has been taken into account following the procedure described by Burakovsky and Preston. The results thus obtained have been found to fit well the Burakovsky-Preston model for the volume dependence of the Grüneisen parameter.

Keywords : Equation of state, tharmoelastic properties, pressure dependence of bulk modulus, Generalized free volume formula, volume dependence of Grüneisen parameter, geophysical minerals.

1. INTRODUCTION

Geophysical minerals are important materials constituted of divalent cations and anions with a predominantly ionic character of the chemical bond between them [1-3]. These compounds have important applications in the field of industry and technology [4-6]. The three geophysical minerals to be considered in the present study are MgO, CaO BaO and Fe_2SiO_4. These solids crystallize with B_1 structure (NaCl type fcc lattice) at ambient conditions of pressure and temperature. At elevated pressures, the geophysical minerals under study exhibit phase transitions [7-10] from B_1 to B_2 structure (CsCl type bcc lattice).

We make use of the Birch-Murnaghan third-order equation of state (EOS) [11] and the Vinet-Rydberg EOS [12] for determining pressure-volume relationships, bulk modulus and its pressure derivative of geophysical minerals with B_1 structure. The two EOSs used in the present study have been applied previously to find the results for different types of solids corresponding to a wide range of compressions [13-16]. The results obtained from the two EOSs are used in the modified version of the generalized free volume formula due to Burakovsky and Preston which takes into account the density or volume dependence of free-volume parameter f or t [17].

2. METHOD OF ANALYSIS

The Birch-Murnaghan third-order EOS can be written as follows [11]

$$P = \frac{3}{2}K_0\left(x^{-7} - x^{-5}\right)\left[1 + \frac{3}{4}\left(K_0' - 4\right)\left(x^{-2} - 1\right)\right] \quad (1)$$

where P is pressure, K_0 and K_0' are the values of bulk modulus and its pressure derivative, respectively, both at zero pressure, and $x = (V/V_0)^{1/3}$.

Equation (1) yields the following expressions for bulk modulus $K = -V\,(dP/dV)$ and its pressure derivative $K' = dK/dP$.

$$K = \frac{1}{2}K_0\left(7x^{-7} - 5x^{-5}\right) + \frac{3}{8}K_0\left(K_0' - 4\right)\left(9x^{-9} - 14x^{-7} + 5x^{-5}\right) \quad (2)$$

and

$$K' = \frac{K_0}{8K}\left[\left(K_0' - 4\right)\left(81x^{-9} - 98x^{-7} + 25x^{-5}\right) + \frac{4}{3}\left(49x^{-7} - 25x^{-5}\right)\right] \quad (3)$$

The corresponding expressions for P, K and K' based on the Vinet-Rydberg EOS [12] are given below

$$P = 3K_0x^{-2}(1-x)\exp\left[\eta(1-x)\right] \quad (4)$$

$$K = K_0x^{-2}\left[1 + \left\{\frac{3}{2}\left(K_0' - 1\right)x + 1\right\}(1-x)\right]\exp\left[\frac{3}{2}\left(K_0' - 1\right)(1-x)\right] \quad (5)$$

and

$$K' = \frac{1}{3}\left[\frac{x(1-\eta) + 2\eta x^2}{1 + (\eta x + 1)(1-x)} + \eta x + 2\right] \quad (6)$$

where $\eta = 3\left(K_0' - 1\right)/2$.

The results for P, K and K' corresponding to different values of volume compression V/V_0 are given in Figures 1-3 and used to determine volume dependence of Grüneisen parameter γ. The Grüneisen parameter gamma is an important parameter related to thermoelastic properties of materials [3]. We have the following relationship [17]

$$\gamma = \frac{\alpha K_T V}{C_V} = \frac{\alpha K_S V}{C_P} \quad (7)$$

where α is thermal expansivity, K_T and K_S isothermal and adiabatic bulk moduli, C_V and C_P are specific heats at constant volume and constant pressure, respectively. Continuous efforts have been made using theoretical models [18-21] for determining volume dependence of γ. The following common formula has been proposed [20]

$$\gamma = \frac{\left(\frac{K'}{2}\right) - \frac{1}{6} - \frac{t}{3}\left(1 - \frac{P}{3K}\right)}{1 - \frac{2t}{3}\left(\frac{P}{K}\right)} \quad (8)$$

where the free volume parameter t = 0 for Slater's formula [18], t = 1 for the formula given by Dugdale and MacDonald [19], t = 2 for the formula by Vashchenko and Zubarev [20], and t = 2.35 taken by Barton and Stacey [21]. Vashchenko and Zubarev have considered three-dimensional oscillations of a lattice with interatomic interactions represented by an anharmonic central potential. Equation (8) has been generalized [22] by taking account of non-central of non-central forces. The generalized free volume formula can be written as follows [17]

$$\gamma = \frac{\left(\frac{K'}{2}\right) - \frac{1}{6} - \frac{t}{3}\left(1 - \frac{P}{3K}\right) + \frac{P}{3K}}{1 - 2t\left(\frac{P}{3K}\right)} \quad (9)$$

Equation (9) takes into account the variation of t with volume or pressure. It is found [17] that value of t varies from t_0 at P = 0 to $t \to 5/2$ in the limit of extreme compression ($V \to 0$ at $P \to \infty$).

At P = 0, Eq. (9) gives

$$\gamma_0 = \left(\frac{K_0'}{2}\right) - \frac{1}{6} - \frac{t_0}{3} \quad (11)$$

Values of γ_0 and K_0' are the Grüneisen parameter and pressure derivative of bulk modulus respectively both at zero-pressure. Values of input data γ_0, K_0' and t_0 are given in Table 1. The results for γ as a function of V/V_0 computed from Eqs. (9) for MgO, CaO, Fe_2SiO_4 and BaO are plotted in Figure 4.

3. RESULTS AND DISCUSSION

Values of pressure P, bulk modulus K and its pressure derivative K' = dK/dP have been computed for AEO compounds using the Birch-Murnaghan third order EOS and the Vinet-Rydberg EOS up to their phase transition ($B_1 \rightarrow B_2$) pressures (P_t). Values of P_t for MgO, CaO, Fe_2SiO_4 and BaO are respectively 250, 61, 30 and 120, all in GPa [24-28]. At pressures below P_t, these solids remain in B_1 crystal structure with face centered cubic lattice. We have performed computations up to the pressures lower than P_t, i.e. for the solids in B_1 structure. The results for P, K and K' are given in Figures 1-3, and compared with the available experimental data [29-34]. The pressure-volume relationships are accurate within one percent, bulk modulus nearly one percent, and pressure derivatives of bulk modulus are uncertain by more than one percent but less than five percent [3, 13, 16]. P and K both increase, but K' decreases with the decreasing V/V_0 (Figures 1-3). The structural phase transition from B1 to B2 crystal structure takes place at $P=P_t$. The fcc arrangement of atoms with six nearest neighbours for B1 structure is transformed to the bcc arrangement with eight nearest neighbour atoms in B2 structure. Consequently, the interatomic separations are changed resulting in modified values of lattice potential energy and free energy responsible for phase transition [1, 3].

Values of γ as a function of volume compression V/V_0 obtained from Eq. (9) are plotted in Figure 4. These results are compared with those determined from the Burakovsky-Preston model based on the formula given below [17]

$$\gamma = \gamma_\infty + a_1\left(\frac{V}{V_0}\right)^{1/3} + a_2\left(\frac{V}{V_0}\right)^{m} \tag{12}$$

where $\gamma_\infty = 1/2, a_1, a_2$ and $m > 1$ are constants for a given material, The simplified B-P model has been used recently [35, 36] by assuming that $a_1=a_2$, and m=1.5. At P=0, $V=V_0$, Eq. (12) gives

$$\gamma_0 = \frac{1}{2} + a_1 + a_2 \tag{13}$$

The assumption $a_1 = a_2 = a$, then yields

$$a = \frac{1}{2}\left(\gamma_0 - \frac{1}{2}\right) \tag{14}$$

The results thus obtained from Eq. (12) for the volume dependence of γ (Figure 4) present close agreement with the corresponding values obtained using the EOSs and the generalized free volume formula (Eq. 9).

4. CONCLUSIONS

The results for P, K, K' and γ for the geophysical minerals have been obtained using the Birch-Murnaghan third order EOS and the Vinet-Rydberg EOS. The calculations have been performed for MgO, CaO, BaO and Fe_2SiO_4 crystallizing with B_1 structure below their phase transition pressures. The computed results are found to present good agreement with the available experimental data. Volume dependence of the Grüneisen parameter has been determined for the solids under study using the generalized free volume formula which takes into account the variation of free volume parameter with change in density. The results obtained in the present study are consistent with the Burakovsky-Preston model for the density dependence of gamma.

Table 1 : Values of input data for alkaline earth oxides [3, 9, 31, 37, 38] used in computations.

	K_0(GPa)	K'_0	γ_0	t_0
MgO	161.6	4.29	1.54	1.32
CaO	110.6	4.85	1.57	2.07
Fe_2SiO_4	201	4.00	1.08	2.26
BaO	74.0	5.67	1.74	2.79

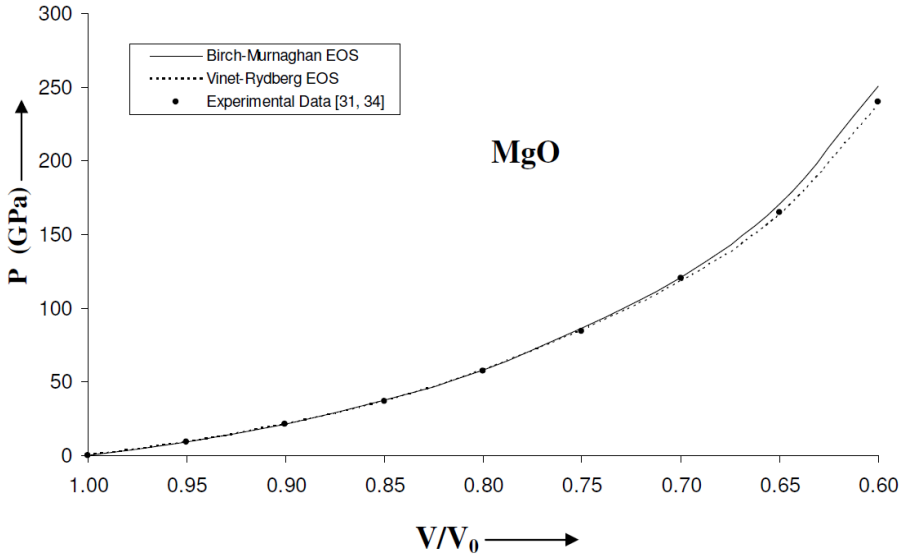

Figure 1(a) : Plots of pressure (P) in GPa versus volume compression (V/V_0) for MgO

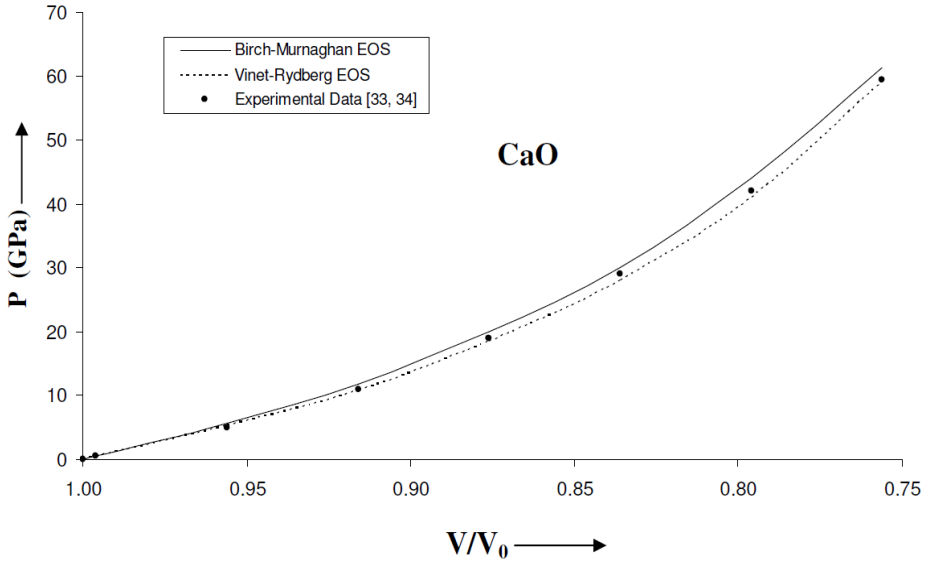

Figure 1(b) : Plots of pressure (P) in GPa versus volume compression (V/V_0) for CaO

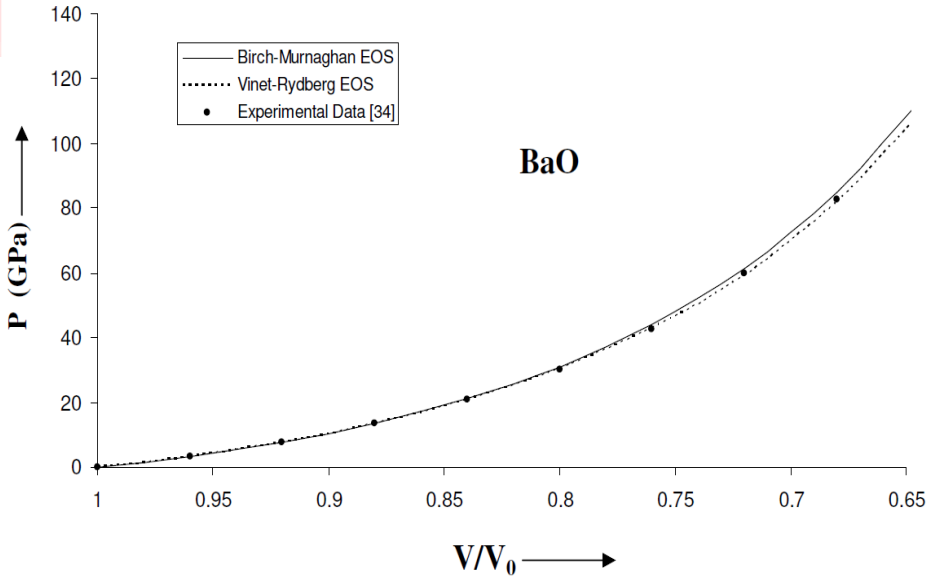

Figure 1(c) : Plots of pressure (P) in GPa versus volume compression (V/V_0) for BaO

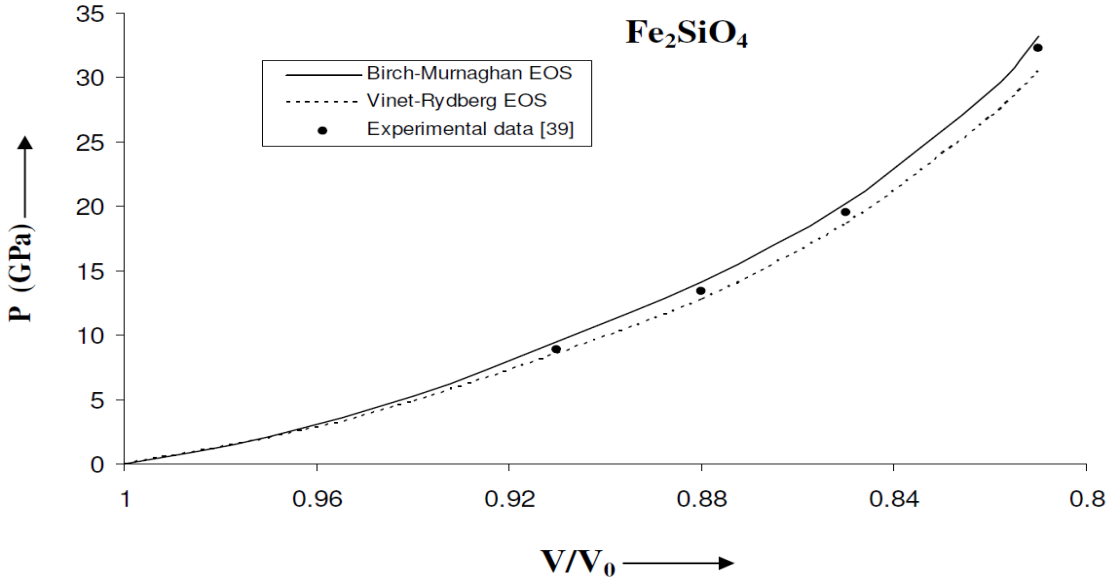

Figure 1(d) : Plots of pressure (P) in GPa versus volume compression (V/V_0) for Fe_2SiO_4

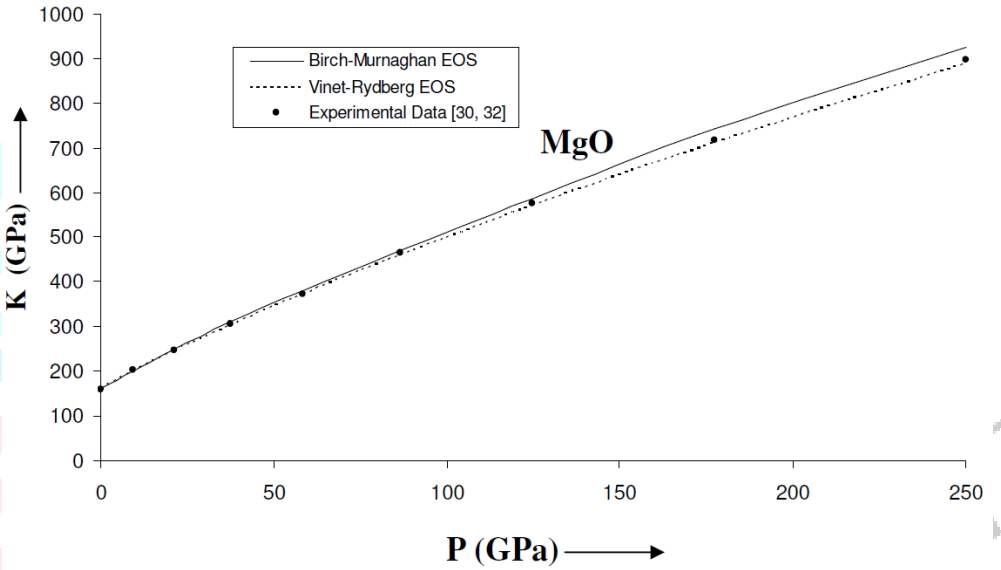

Figure 2(a) : Plots of bulk modulus (K) in GPa versus pressure (P) in GPa for MgO

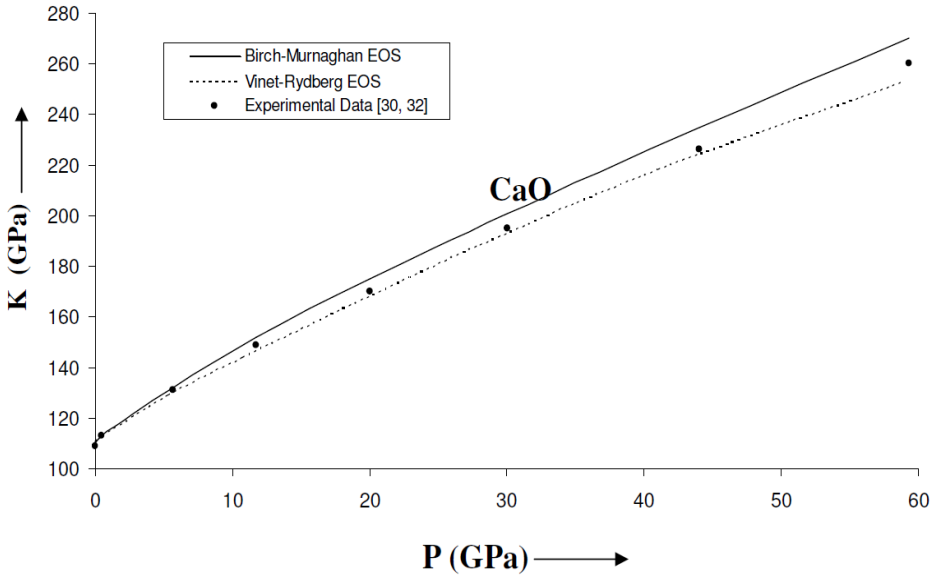

Figure 2(b) : Plots of bulk modulus (K) in GPa versus pressure (P) in GPa for CaO

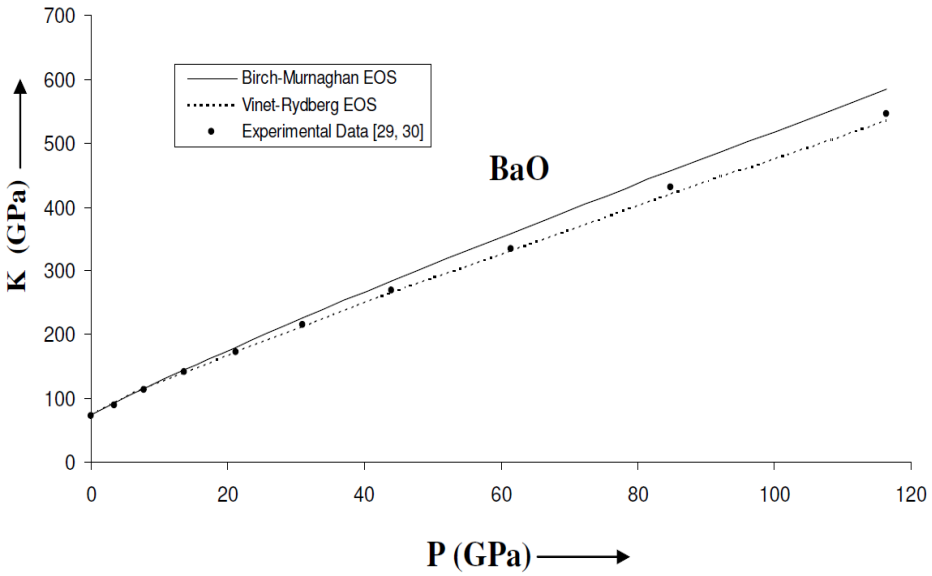

Figure 2(c) : Plots of bulk modulus (K) in GPa versus pressure (P) in GPa for BaO

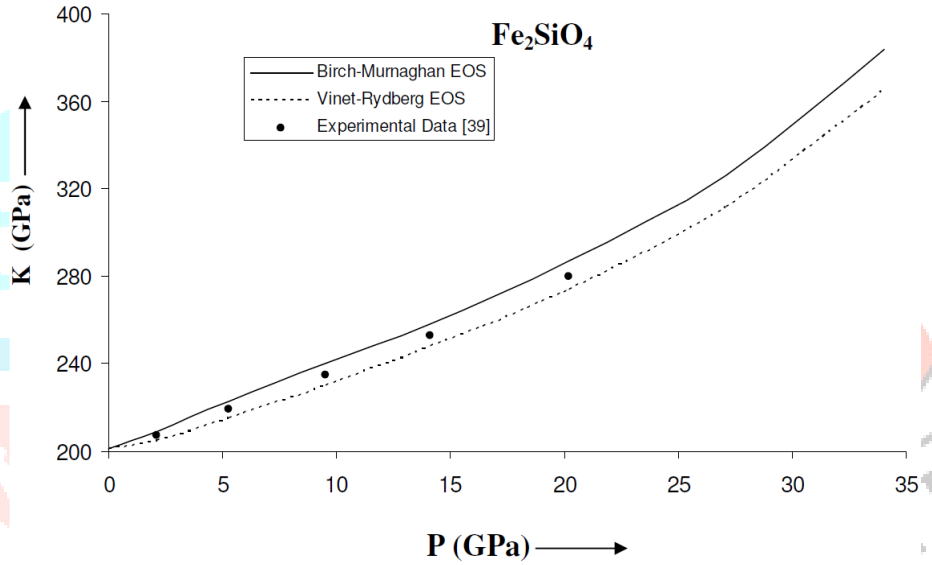

Figure 2(d) : Plots of bulk modulus (K) in GPa versus pressure (P) in GPa for Fe_2SiO_4

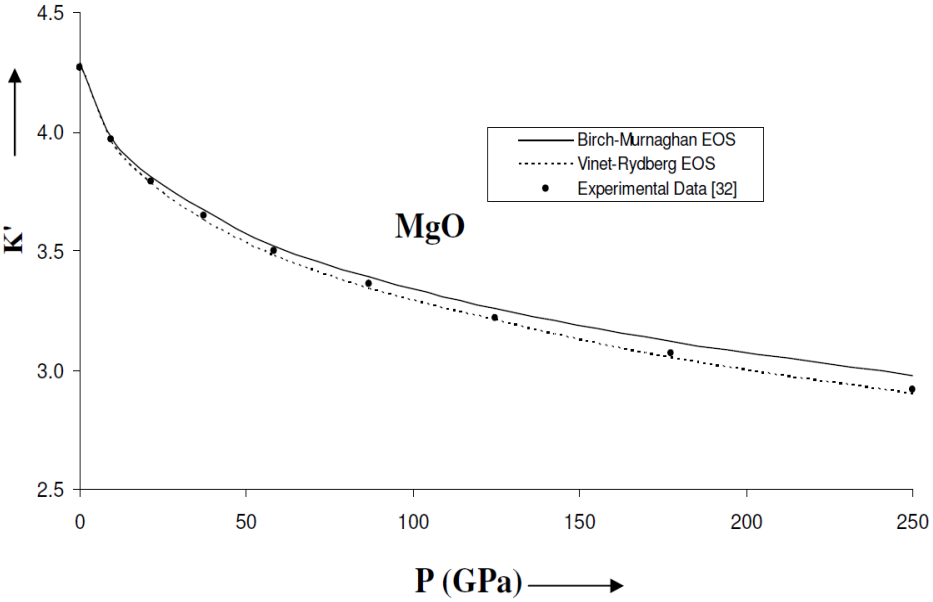

Figure 3(a) : Plots of pressure derivative of bulk modulus (K') versus pressure (P) in GPa for MgO

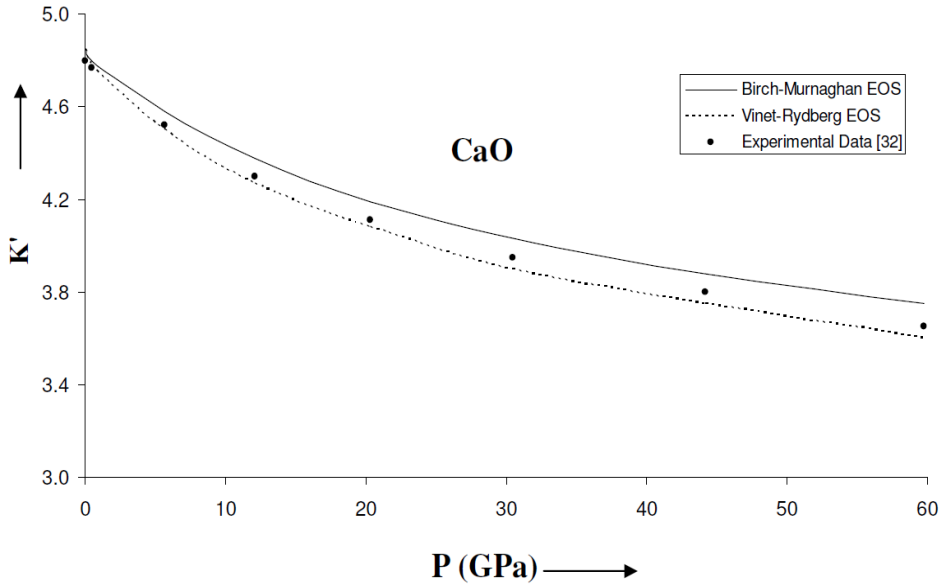

Figure 3(b) : Plots of pressure derivative of bulk modulus (K') versus pressure (P) in GPa for CaO

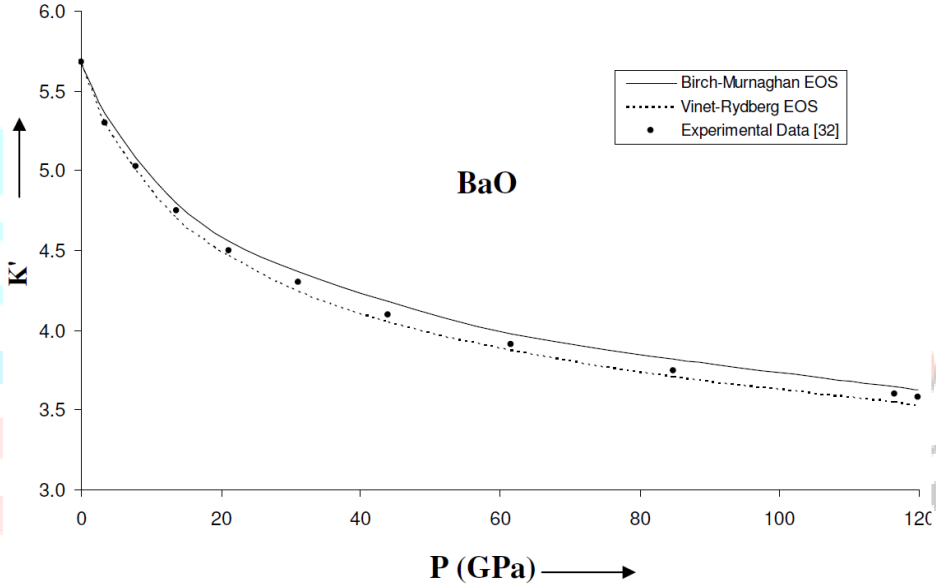

Figure 3(c) : Plots of pressure derivative of bulk modulus (K') versus pressure (P) in GPa for BaO

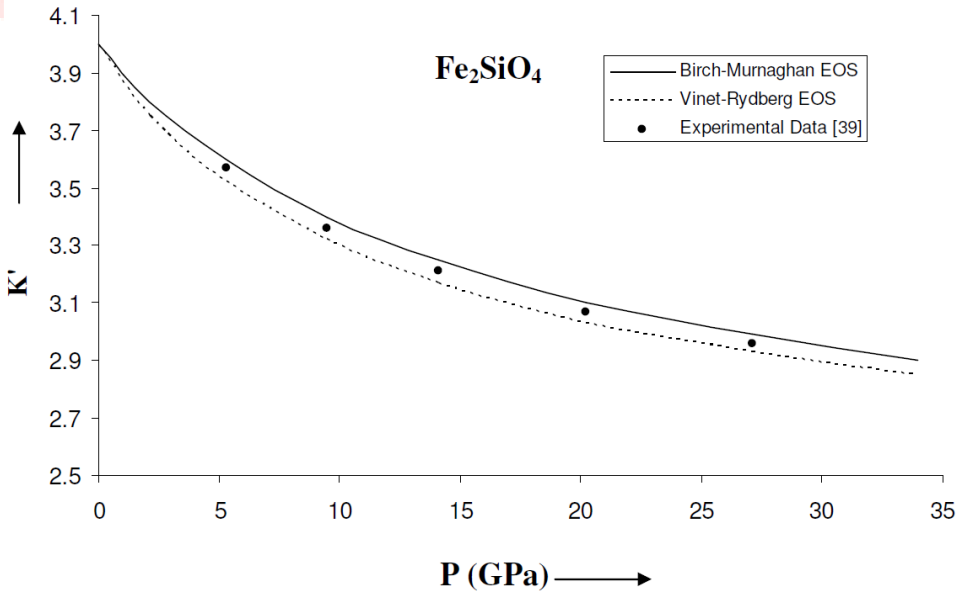

Figure 3(d) : Plots of pressure derivative of bulk modulus (K') versus pressure (P) in GPa for Fe_2SiO_4

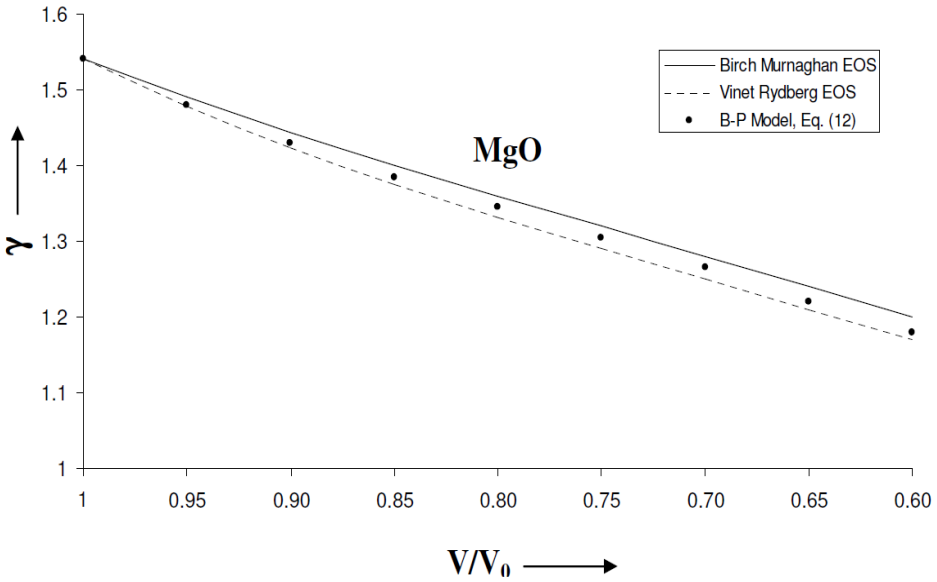

Figure 4(a) : Plots of γ versus volume compression (V/V_0) for MgO

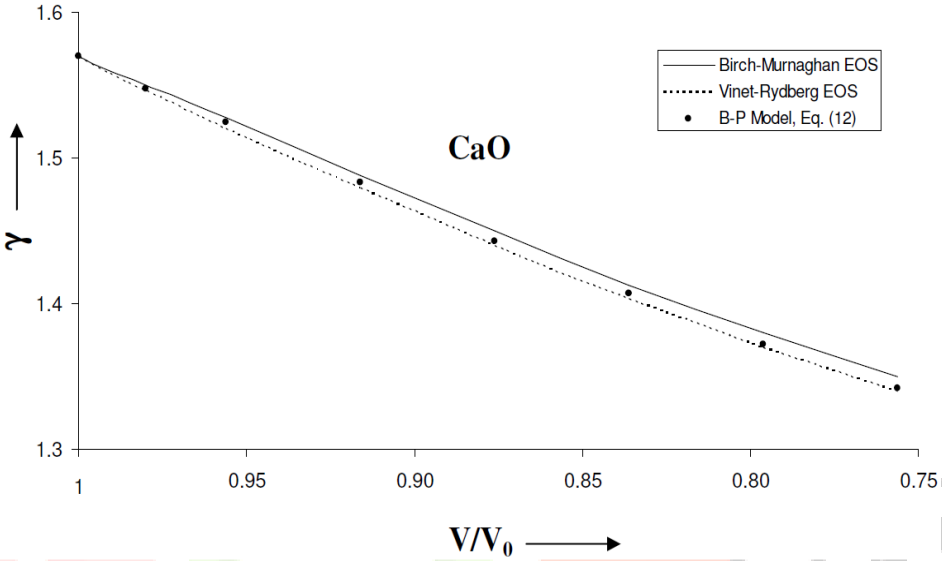

Figure 4(b) : Plots of γ versus volume compression (V/V_0) for CaO

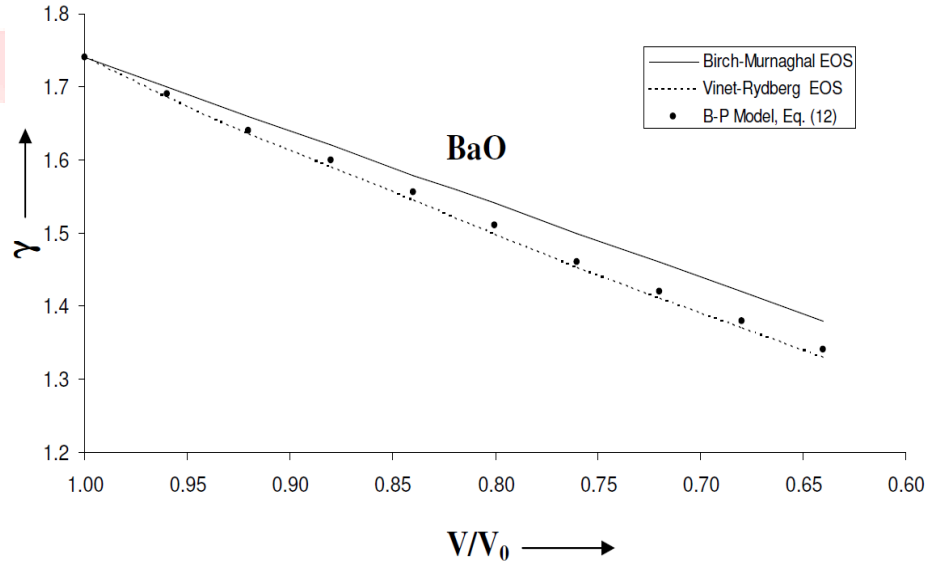

Figure 4(c) : Plots of γ versus volume compression (V/V_0) for BaO

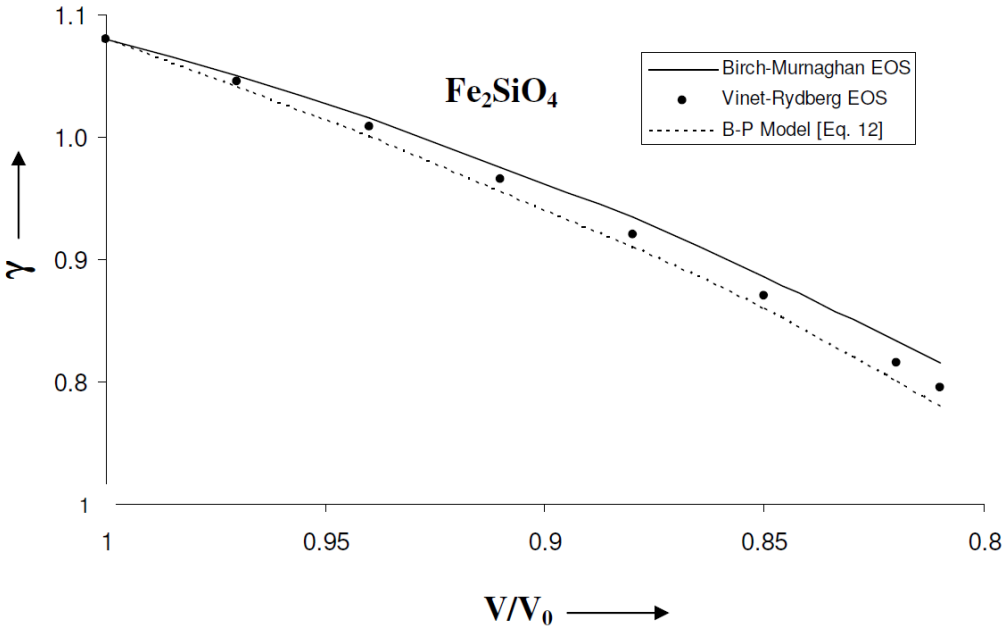

Figure 4(d) : Plots of γ versus volume compression (V/V_0) for Fe_2SiO_4

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