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EQUATION OF STATE FOR THE ANALYSIS OF ELASTIC PROPERTIES OF SILICATE PEROVSKITE

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ABSTRACT

In the present work an attempt has been made for the prediction of suitable equation of state on the basis of computed thermoelastic properties and Gruniesen parameter (γ) of Silicate perovskite i.e. $MgSiO_3$ & $CaSiO_3$ up to the compression range $V/V_0=1$ to $V/V_0= 0.6$, using four different empirical isothermal equations of state viz. Brennan-Stacey EOS, Shanker EOS, Vinet EOS and Kholiya EOS. The critical analysis of obtained results suggest that validity of Shanker EOS and Vinet EOS are most suitable for the determination of elastic constants of Silicate Perovskites while the rest of equation of states viz. Brennan-Stacey EOS and Kholiya EOS are less suitable.

***Key Words*: Compression, Thermoelastic Properties, Gruneisen Parameter, Silicate Perovskites And Equation of State.**

I INTRODUCTION

Silicate perovskite is the term given to (Mg,Fe)SiO_3 (also known as bridgmanite and $CaSiO_3$ (calcium silicate) when arranged in a perovskite structure. Silicate perovskites are mainly found in the lower part of Earth's mantle, between about 670 and 2,700 kilometers. They are thought to form the main mineral phases, together with ferropericlase. During the last year (2014), the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA) approved the name bridgmanite for perovskite-structured (Mg)SiO_3, in honor of physicist Percy Bridgman, who won the Nobel Prize in Physics in 1946 for his high-pressure research.

Silicate perovskite may form up to 93% of the lower mantle [1] and the magnesium form is considered to be the most abundant mineral in the Earth [2]. The highest proposed abundances of silicate perovskites suggest that the lower mantle is richer in silica than the upper mantle and are consistent with the overall chondritic composition of the Earth[3].Under very high pressures of the lowermost mantle, below about 2700 km, the silicate perovskites are replaced by post-perovskite[3]. The physical properties of silicate perovskites under lower mantle conditions, such as seismic velocity, are studied experimentally using laser-heated diamond anvil cells. Naturally occurring silicate perovskites cannot be studied as they are unstable at the Earth's surface [4].

The perovskite structure (first identified in the mineral perovskite) occurs in substances with the general formula ABX_3, where A is a metal that forms large cation, B is another metal that forms smaller cations and X is typically oxygen. The structure may be cubic, but only if the relative sizes of the ions meet strict criteria. Typically, substances with the perovskite structure show lower symmetry, owing to the distortion of the crystal lattice and silicate perovskites in the orthorhombic crystal system[5].

In the present work an attempt has been made to test the validity of suitable equation of state been made for theoretical prediction of elastic properties and Gruneisen parameter for Silicate perovskite i.e. $MgSiO_3$ & $CaSiO_3$ perovskites both at high and low compression ranges using four different isothermal equation of state viz. Vinet EOS, Shanker EOS, Brennan-Stacey EOS and Kholiya EOS. We make use of the formulations for γ and its volume derivatives given by Stacey and Davis to obtain results in case of Silicate perovskite.

II THEORY

An EOS can be derived from the volume derivative of lattice potential energy by using the relation

$$P = -\left(\frac{dW}{dV}\right)_T \quad (1)$$

Where W for an ionic crystal can be written as the sum of electrostatic energy and short range overlap repulsive energy Φ.

Equation of states are derived on taking account of some basic assumptions. Brennan-Stacey EOS[6,7] is based on assumption that Gruniesen parameter is proportional to volume and equation is obtained on account of free volume formula[8],given as follows:

$$P = \frac{3K_0\left(\frac{V}{V_0}\right)^{-\frac{4}{3}}}{\left(3K_0' - 5\right)}\left[\left\{\exp\left(\frac{3K_0' - 5}{3}\right)\left(1 - \frac{V}{V_0}\right)\right\} - 1\right] \quad (2)$$

On the basis of a modified exponential dependence for the short range force constant on volume, the Shanker EOS[9,10] is derived, given as follows:

$$P = \frac{3K_0\left(\frac{V}{V_0}\right)^{-\frac{4}{3}}}{\left(3K_0' - 8\right)}\left[\left\{\left(1 - \frac{1}{t} + \frac{2}{t^2}\right)(\exp ty - 1)\right\} + \left\{y\left(1 + y - \frac{2}{t}\right)\exp ty\right\}\right] \quad (3)$$

Where, $y = 1 - \frac{V}{V_0}$ and $t = K_0' - \frac{8}{3}$

Taking account universal relationship between binding energy and interatomic separation for solids, Vinet EOS [11,12,13] derived given as follows:

$$P = 3K_0 x^{-2}(1 - x)\exp\{\eta(1 - x)\} \quad (4)$$

Where, $x = \left(\frac{V}{V_0}\right)^{\frac{1}{3}}$ and $\eta = \frac{3}{2}\left(K_0' - 1\right)$

Kholiya [14] has expanded pressure in powers of density up to the quadratic term and achieved the EOS as

$$P = \frac{K_0}{2}\left[(K_0' - 3) - 2(K_0' - 2)\left(\frac{V}{V_0}\right)^{-1} + (K_0' - 1)\left(\frac{V}{V_0}\right)^{-2} \right] \quad (5)$$

Isothermal Bulk modulus K_T can be obtained by taking first volume derivative of above three relations as follows:

$$K_T = -V\left(\frac{\partial P}{\partial V}\right)_T \quad (6)$$

Thus taking differentiation of above three pressure-volume relations with respect to volume and putting in equation (4), expressions for isothermal bulk modulus is derived as follows:

$$K_T = \frac{4}{3}P + K_0\left(\frac{V}{V_0}\right)^{-\frac{1}{3}} \exp\left\{\left(K_0' - \frac{5}{3}\right)\left(1 - \frac{V}{V_0}\right)\right\} \quad (7)$$

$$K_T = \frac{4}{3}P + K_0\left(\frac{V}{V_0}\right)^{-\frac{4}{3}} \exp\left\{\left(K_0' - \frac{8}{3}\right)\left(1 - \frac{V}{V_0}\right)\right\} \quad (8)$$

$$K_T = K_0 x^{-2}\left[1 + \{(1 + \eta x)(1 - x)\}\right] \exp\ \eta(1 - x) \quad (9)$$

$$K_T = K_0 (K_0' - 2)\left(\frac{V}{V_0}\right)^{-1}\left[\left(\frac{K_0' - 1}{K_0' - 2}\right)\left(\frac{V}{V_0}\right)^{-1} - 1\right] \quad (10)$$

Pressure derivative of isothermal bulk modulus K_T gives first pressure derivative of bulk modulus K_T' as follows:

$$K_T' = \frac{16}{9}\frac{P}{K_T} + \left(1 - \frac{4}{3}\frac{P}{K_T}\right)\left[\left\{\left(K_0' - \frac{5}{3}\right)\left(\frac{V}{V_0}\right)\right\} + \frac{5}{3}\right] \quad (11)$$

$$K_T' = \frac{16}{9}\frac{P}{K_T} + \left(1 - \frac{4}{3}\frac{P}{K_T}\right)\left[\left\{\left(K_0' - \frac{8}{3}\right)\left(\frac{V}{V_0}\right)\right\} + \frac{8}{3}\right] \quad (12)$$

$$K_T' = \frac{1}{3}\left[\frac{x(1 - \eta) + 2\eta x^2}{1 + (\eta x + 1)(1 - x)} + \eta x + 2\right] \quad (13)$$

$$K_T' = \frac{(K_0' - 2)\left(\frac{V}{V_0}\right) - 2(K_0' - 1)}{(K_0' - 2)\left(\frac{V}{V_0}\right) - (K_0' - 1)} \quad (14)$$

Equations (2), (7) and (11) corresponds to Brennan-Stacey EOS. Equation (3), (8) and (12) corresponds to Shanker EOS. Equations (4), (9) and (13) corresponds to Vinet EOS and (5), (10) and (14) correspond to Kholiya EOS. In the above equations K_0 is isothermal bulk modulus and K_0' is the first pressure derivative of isothermal bulk modulus at zero pressure value.

All these EOS are also tested for the basic criteria which must be satisfied by an EOS for its validity and applicability as suggested by Stacey [14, 15, 16]. These criteria are as follow;

(1) In the limit $P \to \infty$, $\frac{V}{V_0} \to 0$.

(2) With the increase in pressure isothermal bulk modulus must increase continuously and in the limit of infinite pressure $K_T \to \infty$.

(3) K_T' must decrease progressively with the increase in pressure such that K_T' remains greater than 5/3 in the limit of infinite pressure.

Gruniesen parameter γ derived by Barton-Stacey [17, 18] is given by following expression:

$$\gamma = \frac{\frac{1}{2}K_T' - \frac{1}{6} - \frac{f}{3}\left(1 - \frac{P}{3K_T}\right)}{\left(1 - \frac{4}{3}\frac{P}{K_T}\right)} \tag{15}$$

Where, f =2.35 a constant, K_T is isothermal bulk modulus and K_T' is the first pressure derivative of isothermal bulk modulus.

III RESULT AND DISCUSSION

In the present work we have computed the pressure P, isothermal bulk modulus K_T, first pressure derivative of isothermal bulk modulus K_T', and Gruneisen parameter for $MgSiO_3$ & $CaSiO_3$ perovskites. In This calculation we have used four different EOS viz Brennan-Stacey EOS, Shanker EOS, Vinet EOS & Kholiya EOS. The expressions of P for these EOS are given in equations 2, 3, 4 and 5 respectively. K_T for these EOS is computed by using equations 7, 8, 9 and 10 respectively. The value of K_T' is obtained by using equations 11, 12, 13 and 14 respectively. Using different parameters corresponding to the different EOS required in equation 15 the Gruneisen parameter has been calculated. Input parameters are given in Table-1. The calculated values of elastic parameters P, K_T, K_T' and γ are given in Table-2 &3 for $MgSiO_3$ perovskite and Table-4 &5 for $CaSiO_3$ perovskite. Graphs are plotted for P vs V/V_0, K_T vs P, K_T' vs P and γ vs V/V_0 for $MgSiO_3$ perovskite are given in Fig.1 to Fig. 4 and the plots for P vs V/V_0, K_T vs P, K_T' vs P and γ vs V/V_0 for CaSiO3 perovskites are given in Fig.5 to Fig. 8. The critical analysis of the graphs suggests that $P \to \infty$, $\frac{V}{V_0} \to 0$ clearly evident from Fig. (1) & from Fig. (5). From the Fig. (2 & 6) it is observed that with the increase in pressure in terms of compression ratio, isothermal bulk modulus increases continuously. Fig. (3 & 7) shows that K_T' decreases as the pressure P gets increased. It verifies the constraint which states that the pressure derivative of isothermal bulk modulus must decreases progressively with the increase in pressure.

Again analyzing the graph plotted between V/V_0 vs γ by using different isothermal EOS as shown in Fig. (4 & 8), it is observed that the variation of elastic parameters such as K_T , K_T' and pressure for MgSiO3 & CaSiO3 perovskites are well satisfied by all four different EOS viz Brennan-Stacey EOS, Shanker EOS, Vinet EOS & Kholiya EOS used in present computation. For better approximation graph between γ vs Ω (V/V_0) must be a straight line[19] .On the observation of slope of graphs between V/V0 vs γ (Fig.4 & Fig.8) it is clear that Shanker EOS and Vinet EOS are most suitable for the determination of elastic constants of Perovskites while the rest of equation of states viz. Brennan-Stacey EOS and Kholiya EOS are less suitable.

Table-1 Input parameters [20]

Mineral	K_0(GPa)	K'_0
MgSiO3 Perovskite	261	4.0
CaSiO3 Perovskite	232	4.8

Table-2 Calculated values of P & KT at different compression for MgSiO3 Perovskite

V/V0	P(VEOS)	P(B-S)	P(Shnkr)	P(Kholiya)	K_T(Vinet)	K_T(B-S)	K_T (Shnkr)	K_T (Kholiya)
1	0	0	0	0	261	261	261	261
0.95	14.82	14.82	14.83	14.82	318.29	318.12	318.51	318.12
0.9	33.86	33.83	33.88	33.83	387.35	386.48	388.39	386.67
0.85	58.34	58.22	58.42	58.25	471.1	468.62	473.82	469.62
0.8	89.92	89.57	90.11	89.72	573.35	567.77	578.99	570.94
0.75	130.89	130.01	131.21	130.5	699.13	688.13	709.5	696
0.7	184.37	182.44	184.8	183.77	855.26	835.2	872.85	852.24
0.65	254.82	250.9	255.16	254.05	1051.04	1016.36	1079.41	1050.18
0.6	348.61	341.05	348.38	348	1299.46	1241.66	1343.66	1305

Table-3 Calculated values of K'_T & γ (Gruneisen Parameter) at different compression (V/V_0) of $MgSiO_3$

V/V_0	K'_T(Vinet)	K'_T(B-S)	K'_T(Shnkr)	K'_T(Kholiya)	γ (VEOS)	γ (B-S)	γ (Shnkr)	γ (Kholiya)
1	4	4	4	4	1.05	1.05	1.05	1.05
0.95	3.77	3.72	3.77	3.73	1.01	0.99	1.01	0.99
0.9	3.57	3.48	3.57	3.5	0.97	0.92	0.97	0.93
0.85	3.38	3.27	3.39	3.31	0.93	0.86	0.93	0.88
0.8	3.22	3.07	3.24	3.14	0.88	0.79	0.89	0.84
0.75	3.06	2.89	3.09	3	0.84	0.73	0.85	0.8

0.7	2.92	2.73	2.96	2.88	0.79	0.66	0.82	0.76
0.65	2.78	2.57	2.84	2.76	0.74	0.6	0.78	0.73
0.6	2.65	2.43	2.73	2.67	0.7	0.53	0.74	0.7

Table-4 Calculated Values of P & K_T at different compression for $CaSiO_3$ Perovskite

V/V0	P(Vinet)	P(B-S)	P(ShnkrEOS)	P(Kholiya)	K_T(VEOS)	K_T(B-S)	K_T(Shnkr)	K_T(Kholiya)
1	0	0	0	0	232	232	232	232
0.95	13.45	13.45	13.45	13.43	294.03	293.96	294.32	293.05
0.9	31.37	31.36	31.41	31.22	370.99	370.52	372.36	366.62
0.85	55.24	55.17	55.37	54.67	467.04	465.43	470.63	455.97
0.8	87.11	86.87	87.42	85.55	587.77	583.57	595.19	565.5
0.75	129.84	129.17	130.41	126.31	740.71	731.12	754.24	701.16
0.7	187.48	185.84	188.35	180.39	936.28	916.88	959.03	871.18
0.65	265.94	262.24	266.94	252.73	1189.77	1151.56	1225.29	1087.24
0.6	373.93	366.07	374.4	350.58	1519.97	1451.38	1575.38	1366.22

Table-5 Calculated Values of K'_T & γ (Gruneisen parameter) for CaSiO3 Perovskite

V/V_0	K'_T(VEOS)	K'_T(B-S)	K'_T(Shnkr)	K'_T(Kholiya)	γ (VEOS)	γ (B-S)	γ (Shnkr)	γ (Kholiya)
1	4.8	4.8	4.8	4.8	1.45	1.45	1.45	1.45
0.95	4.48	4.44	4.49	4.33	1.39	1.37	1.39	1.31
0.9	4.21	4.13	4.22	3.97	1.32	1.28	1.33	1.19
0.85	3.97	3.86	3.99	3.68	1.26	1.2	1.27	1.09
0.8	3.75	3.61	3.78	3.44	1.2	1.11	1.22	1.01
0.75	3.56	3.38	3.59	3.24	1.14	1.03	1.16	0.94
0.7	3.38	3.18	3.42	3.07	1.08	0.95	1.1	0.88
0.65	3.21	2.98	3.26	2.92	1.02	0.86	1.04	0.83
0.6	3.06	2.8	3.12	2.79	0.96	0.78	0.98	0.78

Fig.1 P vs V/V0 for $MgSiO_3$ Perovskite

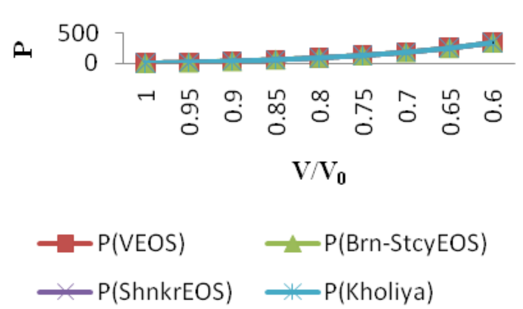
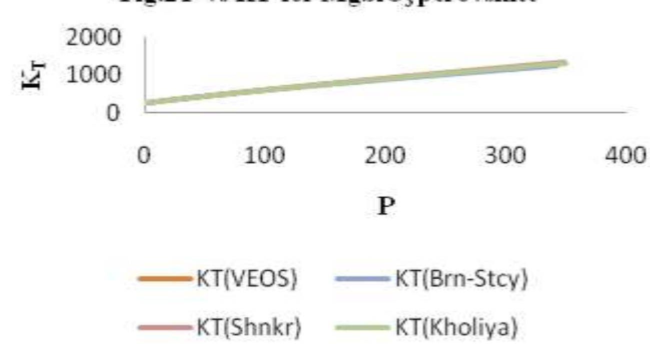


Fig.2 P vs KT for $MgSiO_3$ perovskite



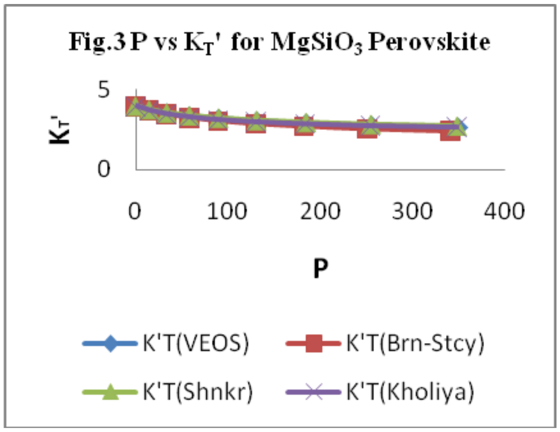


Fig.3 P vs K_T' for $MgSiO_3$ Perovskite

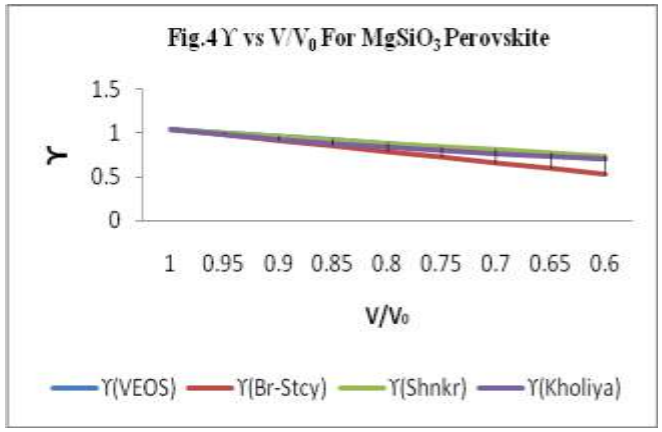


Fig.4 Υ vs V/V_0 For $MgSiO_3$ Perovskite

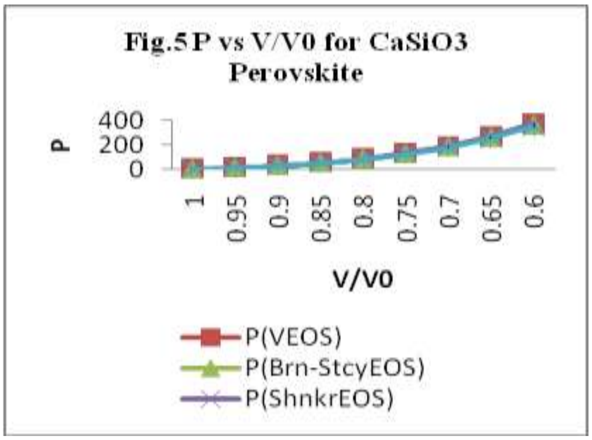


Fig.5 P vs V/V0 for CaSiO3 Perovskite

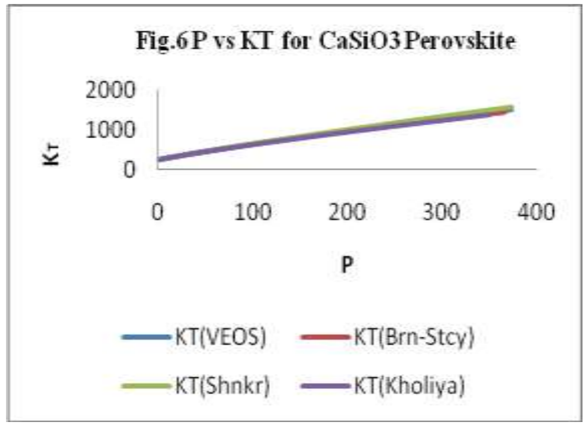


Fig.6 P vs KT for CaSiO3 Perovskite

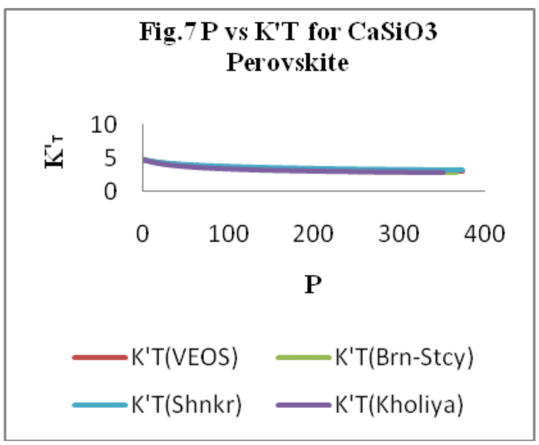


Fig.7 P vs K'T for CaSiO3 Perovskite

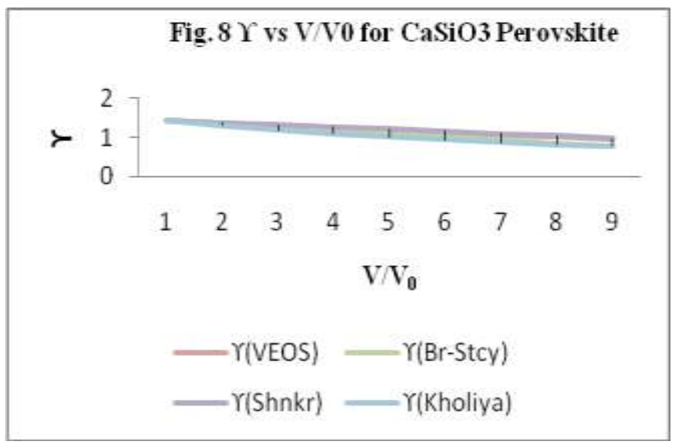


Fig. 8 Υ vs V/V0 for CaSiO3 Perovskite

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