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Pressure – Volume Behavior of Mgo At Elevated Temperatures And Pressure

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ABSTRACT

The isothermal equations of state (EOS) of solids have played an important role in the field of high-pressure physics. An isothermal EOS is used to study the relationship between pressure P and volume compression at a given temperature. Equation of state is also used to study the isothermal bulk modulus BT and its pressure derivatives Bo` and Bo``, respectively. These derivatives are used as input parameters in various phenomenological forms. The values of Bo`` for various solids are much less accurate as compared to the values of B T and Bo`. In the present work we consider six different forms of EOS which contain B T and Bo` only. Using these forms we have studied the pressure-volume relationships for MgO at room temperature and also at elevated temperatures (500-1500 K). Periclase is the end member of the (Mg, Fe) O solid solution series. A precise description of the pressure, volume and temperature (P_V_T) relationship of MgO is therefore essential.

KEYWORDS   Equation of State (EOS), Isothermal Bulk Modulus, Isothermal Pressure Derivatives

Introduction

MgO has low chemical reactivity and it is stable in a large pressure and temperature range, which makes it an ideal pressure calibrant. Values of B_T and $B_o`$ estimated corresponding to different temperatures is used appropriately as input data. Isaak et al. [1] have determined the thermo elastic properties of MgO at high temperatures and high pressure using the potential induced breathing (PIB) electron gas model based on the first principles approach. The ab-initio method of Isaak et al. is based on the detailed calculations of the Helmholtz energy F versus volume at constant temperature T at selected temperatures. By taking the appropriate derivatives of F, values of pressure P, isothermal bulk modulus BT and its pressure derivative Bo` are numerically determined. The results thus obtained have been found to present good agreement with the measurements of the temperature dependence of thermo elastic properties [2, 3]. The values of P, BT and Bo` for MgO at 500, 1000 and 1500 and down to a compression of V/V0=0.60 determined by Isaak et al. have been reported in the tabular form by Anderson [4].

The various phenomenological forms for the isothermal equation of state are given below for ready reference

$$P = \frac{B_0}{(B_0`+1)}\left[\left\{\exp\left(B_0`+1\right)\left(1 - \frac{V}{V0}\right)\right\} - 1\right]$$

$$B_T = B_0\left(\frac{V}{V_0}\right)\exp\left[(B_0`+1)\left(1 - \frac{V}{V_0}\right)\right]$$

$$B_T` = (B_0`+1)\frac{V}{V_0} - 1$$

The above equation is the usual Tait equation (UTE) frequently reported in the literature [6, 7,9,11]. The UTE has been reproduced recently by Kumar [12] using the Chopelas-Boehler relationship [13] according to which $(\delta_T +1)$ varies as V/V_0, and taking the Anderson Gruneisen parameter $\delta_T = dKT/dP$ [14].

$$P = \left[\frac{3B_0\left(\frac{V}{V_0}\right)^{\frac{-4}{3}}}{(3B_0`-5)}\right]\left[\exp\left\{\left(\frac{3B_0`-5}{3}\right)\left(1 - \frac{V}{V_0}\right)\right\} - 1\right]$$

$$B_T = B_0\left(\frac{V}{V_0}\right)^{\frac{-1}{3}}\exp\left\{\left(B_0` - \frac{5}{3}\right)\left(1 - \frac{V}{V_0}\right)\right\} + \frac{4}{3}P$$

$$B_T` = \left(1 - \frac{4}{3}\frac{P}{B_T}\right)\left[\left(B_0` - \frac{5}{3}\right)\frac{V}{V_0} + \frac{5}{3}\right] + \frac{16}{9}\frac{P}{B_T}$$

The above equation is the well known Born Mie equation based on an inverse power form for the short-range repulsive potential energy [4, 15].]

$$P = \left[\frac{3B_0\left(\frac{V}{V_0}\right)^{\frac{-4}{3}}}{(3B_0`-5)}\right]\left[\exp\left\{\left(\frac{3B_0`-5}{3}\right)\left(1 - \frac{V}{V_0}\right)\right\} - 1\right]$$

$$B_T = B_0\left(\frac{V}{V_0}\right)^{\frac{-1}{3}}\exp\left\{\left(B_0` - \frac{5}{3}\right)\left(1 - \frac{V}{V_0}\right)\right\} + \frac{4}{3}P$$

$$B_T` = \left(1 - \frac{4}{3}\frac{P}{B_T}\right)\left[\left(B_0` - \frac{5}{3}\right)\frac{V}{V_0} + \frac{5}{3}\right] + \frac{16}{9}\frac{P}{B_T}$$

The above equation is the BrennanStacey equation [6, 16] derived using the free volume formula for the Gruneisen parameter and taking the second Gruneisen constant **q**=1.

$$P = \frac{B_0\left(\frac{V}{V_0}\right)^{\frac{-4}{3}}}{t}\left[1 - \frac{1}{t} + \frac{2}{t^2}\right)(\exp(ty-1) + y\left(1 + y - \frac{2}{t}\right)\exp(ty)]$$

$$B_T = B_0\left(\frac{V}{V_0}\right)^{\frac{-1}{3}}(1 + y + y^2)\exp(ty) + \frac{4}{3}p$$

$$B_T` = \frac{4}{3} + \left(1 - \frac{4}{3}\frac{P}{B_T}\right)\left[\frac{1}{3} + \frac{V}{V_0}\left\{t + \frac{(1+2y)}{(1+y+y^2)}\right\}\right]$$

Where $t = B_0` - \left(\frac{8}{3}\right)$

The above equation is the Shanker equation derived using a combined form of inverse power dependence and an exponential dependence for the short-range force constant on volume [17].

$$P = 3\frac{(1-X)B_0}{X^2}\exp\left\{\eta(1-X)\right\}$$

The above equation is the Vinet equation of state [18, 19] based on an expression for the cohesive energy of a condensed system that is assumed to vary only as a function of a normalized inter-particle separation *r*. The interatomic interaction in solids related mainly to compression was expressed

by a form A (1+ar) exp(-br) with A, a and b as material constants. This form leads to the derivation of the Vinet equation of state.

$$P = \frac{3}{2} B_0 (x^{-7} - x^{-5})[1 + \frac{3}{4} A_1 (x^{-2} - 1)]$$

$$B_T = \frac{1}{2} B_0 (7x^{-7} - 5x^{-5}) + \frac{3}{8} B_0 A_1 (9x^{-9} - 14x^{-7} + 5x^{-5})$$

$$B_T^{'} = \frac{B_0}{8B_T}[(B_0^{'} - 4)(81x^{-9} - 98x^{-7} + 25x^{-5}) + \frac{4}{3}(49x^{-7} - 25x^{-5})]$$

The above equation is the Birch Murnaghan third-order EOS widely used in geophysics and high-pressure physics [4-6]. This equation is based on the finite strain theory [20]. Stacey et al. [6, 21] have shown that Birch Murnaghan third-order EOS may also be derived from a potential function expressed as the sum of three inverse power terms.

Result and Discussion:
For studying the pressure-volume relationships at high temperatures we need the input parameters B_T and $B_o^{'}$ corresponding to these temperatures. We use the ab-initio values at $P''0$ obtained by Isaak et al. [1] for MgO at 500, 1000 and 1500K as reported by Anderson [4]. These are given in Table 1 and used as input for all the equations of state under study without making any adjustment or fitting.

Table 1 Values of input data for MgO

Temperature (K)	(GPa)	
500	175	4.21
1000	160	4.36
1500	144	4.53

The results for pressure P, isothermal bulk modulus B_T and pressure derivative $B_T^{'}$ obtained from different equations are compared. The comparison reveals that the Vinet EOS and the Shanker EOS yield very similar results.

The values of pressure P (GPa) for MgO at different compressions and temperatures have been calculated using Usual Tait Equation of State (A), Born Mie Equation of State (B), Shankar Equation of State (C), Vinet Equation of State (D) and Birch-Murnaghan Equation of State (E) in the tables 2-4, given below.

Table 2 Values of Pressure P (GPa) for MgO at different compressions at T=500 K

V/Vo	A(P)	B(P)	C(P)	D(P)	E(P)
1	0	0	0	0	0
0.9	23	23.1	23	23	23
0.8	61.6	62.8	61.8	61.7	62.6
0.7	127	134	128	128	133
0.6	236	267	245	246	265

Table 3 Values of Pressure P (GPa) for MgO at different compressions at T=1000K

V/Vo	A(P)	B(P)	C(P)	D(P)	E(P)
1	0	0	0	0	0
0.9	21.2	21.2	21.2	21.1	21.2
0.8	57.4	58.4	57.4	57.3	58.3
0.7	119	126	120	120	125
0.6	225	257	232	233	253

Table 4 Values of Pressure P (GPa) for MgO at different compressions at T=1500K

V/Vo	A(P)	B(P)	C(P)	D(P)	E(P)
1	0	0	0	0	0
0.9	19.2	19.3	19.2	19.2	19.3
0.8	52.7	53.7	52.7	52.5	53.5
0.7	111	117	112	111	116
0.6	212	243	218	218	238

The values of isothermal bulk modulus B_T(GPa) for MgO at different compressions and temperatures have been calculated using Usual Tait Equation of State(A), Born Mie Equation of State (B), Shankar Equation of State (C), Vinet Equation of State (D) and Birch-Murnaghan Equation of State (E) in the tables 5-7, given below.

Table 5 Values of isothermal bulk modulus B_T(GPa) for MgO at different compressions at T=500 K

V/Vo	A(B_T)	B(B_T)	C(B_T)	D(B_T)	E(B_T)
1	175	175	175	175	175
0.9	265	268	266	265	267
0.8	397	416	403	399	414
0.7	585	667	619	602	658
0.6	844	1119	968	937	1092

Table 6 Values of isothermal bulk modulus B_T (GPa) for MgO at different compressions at T=1000K

V/Vo	A(B_T)	B(B_T)	C(B_T)	D(B_T)	E(B_T)
1	160	160	160	160	160
0.9	246	248	246	246	248
0.8	374	392	379	375	390
0.7	559	639	588	576	630
0.6	819	1093	932	902	1064

Table 7 Values of isothermal bulk modulus B_T (GPa) for MgO at different compressions at T=1500K

V/Vo	A(B_T)	B(B_T)	C(B_T)	D(B_T)	E(B_T)
1	144	144	144	144	144
0.9	225	227	225	225	227
0.8	348	366	352	348	362
0.7	530	607	553	542	595
0.6	789	1067	890	861	1025

The values of pressure derivative of isothermal bulk modulus (GPa) for MgO at different compressions and temperatures have been calculated using Usual Tait Equation of State(A), Born Mie Equation of State (B), Shankar Equation of State (C), Vinet Equation of State (D) and Birch-Murnaghan Equation of State (E) in the tables 8-10 given below.

**Table 8 Values of pressure derivative of isothermal bulk modulus $B_T^{'}$ (GPa) for MgO at different compressions at T=500 K**

V/Vo	A(B_T)	B (B_T)	C(B_T)	D(B_T)	E(B_T)
1	4.21	4.21	4.21	4.21	4.21
0.9	3.69	3.88	3.74	3.69	3.86
0.8	3.17	3.63	3.38	3.3	3.58
0.7	2.65	3.334	3.08	2.97	3.38
0.6	2.13	3.29	2.83	2.7	3.21

Table 9 Values of pressure derivative of isothermal bulk modulus $B_T^`$ (GPa) for MgO at different compressions at T=1000K

V/Vo	A ($B_T^`$)	B($B_T^`$)	C($B_T^`$)	D($B_T^`$)	E($B_T^`$)
1	4.36	4.36	4.36	4.36	4.36
0.9	3.82	4.02	3.86	3.81	3.98
0.8	3.29	3.76	3.48	3.337	3.7
0.7	2.75	3.56	3.16	3.06	3.49
0.6	2.22	3.41	2.9	2.77	3.33

Table 10 Values of pressure derivative of isothermal bulk modulus $B_T^`$ (GPa) for MgO at different compressions at T=1500K

V/Vo	A($B_T^`$)	B($B_T^`$)	C($B_T^`$)	D($B_T^`$)	E($B_T^`$)
1	4.53	4.53	4.53	4.53	4.53
0.9	4.17	4.36	4.17	4.11	4.3
0.8	3.59	4.08	3.74	3.55	3.99
0.7	3.02	3.88	3.39	3.28	3.75
0.6	2.44	3.73	3.09	2.96	3.56

The values of pressure P(GPa) for MgO at different compressions and temperatures have been plotted using Usual Tait Equation of State (Series1), Born Mie Equation of State (Series2), Shankar Equation of State (Series3), Vinet Equation of State (Series4) and Birch-Murnaghan Equation of State (Series5) in the graphs 2-4, given below.
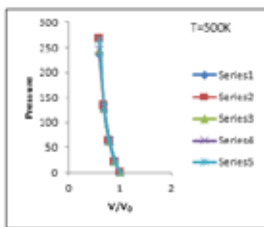
Figure 2 Pressure P(GPa) versus V/V₁ for MgO at T=500K
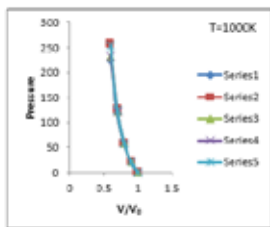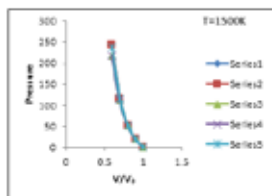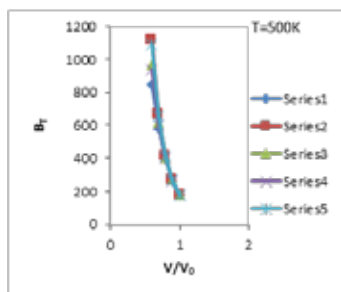
Figure 3 Pressure P(GPa) versus V/V₀ for MgO at T=1000K

Figure 4 Pressure P(GPa) versus V/V₁ for MgO at T=1500K

The values of Isothermal bulk modulus B_T (GPa) for MgO at different compressions and temperatures have been plotted using Usual Tait Equation of State (Series1), Born Mie Equation of State (Series2), Shankar Equation of State (Series3), Vinet Equation of State (Series4) and Birch-Murnaghan Equation of State (Series5) in the graphs 5-7, given below.

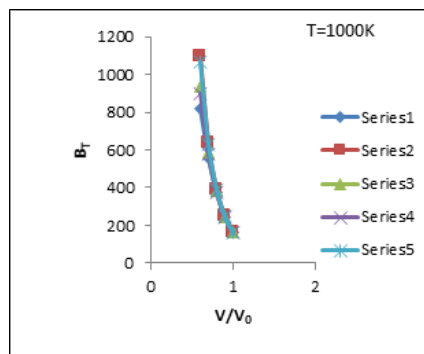**Figure 5 Isothermal bulk modulus BT (GPa) versus V/ V0 for MgO at T=500K**

Figure 6 Isothermal bulk modulus BT (GPa) versus V/ V0 for MgO at T=1000K
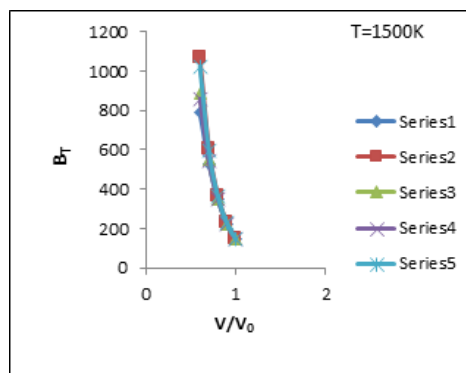

Figure 7 Isothermal bulk modulus BT (GPa) versus V/ V0 for MgO at T=1500K

The values of pressure derivative of isothermal bulk modulus $B_T^`$ (GPa) for MgO at different compressions and temperatures have been plotted using Usual Tait Equation of State (Series1), Born Mie Equation of State (Series2), Shankar Equation of State (Series3), Vinet Equation of State (Series4) and Birch-Murnaghan Equation of State (Series5) in the graphs 8-10, given below.
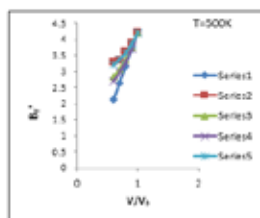

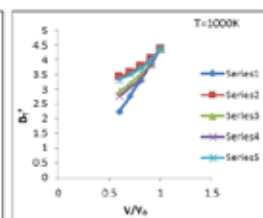Figure 8 Pressure derivative of isothermal bulk modulus B_T (GPa) versus V/V₁ for MgO at T=500K

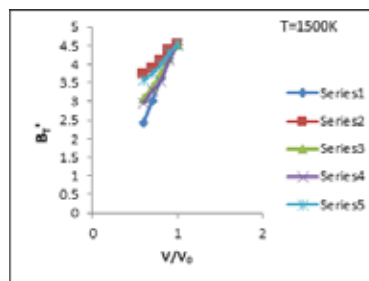Figure 9 Pressure derivative of isothermal bulk modulus B_T (GPa) versus V/V₀ for MgO at T=1000K

Figure 10 Pressure derivative of isothermal bulk modulus BT` (GPa) versus V/ V0 for MgO at T=1500K

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