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Analysis of volume dependence of Grüneisen ratio of Forsterite

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The purpose of the present paper is to derive a new empirical relationship for the volume dependence of Grüneisen ratio (γ) by using simple and straightforward approach. The results thus obtained for Forsterite (Mg_2SiO_4) from the two different methods are identical to each other. Consistency of calculated values with those values compiled by Cynn H, Carnes J D, Anderson O L, J Phys Chem Sol, 57 (1996) 1593 reveals the validity of the formulation. It is also found that the heat capacity does not influence the change in (γ) with the volume ratios in the studied range.

Keywords: Grüneisen ratio, Anderson-Grüneisen parameter, Thermoelastic properties, Forsterite

1 Introduction

Grüneisen ratio (γ) is a very important parameter used to quantify the relationship between thermal and elastic properties of solids. The Grüneisen ratio (γ) can be considered as a measure of the change of pressure resulting from the increase energy density at constant volume[1]. Grüneisen ratio (γ) is useful to investigate the anharmonic property of materials. There is a long standing interest in the behaviour of the Grüneisen ratio (γ) at high pressure or compression because of its importance in geophysics, thermodynamics and condensed matter physics[2]. The Grüneisen ratio (γ) has both a microscopic and macroscopic definitions. Vibrational Grüneisen ratio (γ_i)[3] may be defined as the logarithmic volume derivative of phonon frequency, ω_i, i.e.:

$$\gamma_i = -\frac{\partial \ln \omega_i}{\partial \ln V} \qquad \text{... (1)}$$

and the thermodynamic Grüneisen ratio (γ_{th})[4]:

$$\gamma_{th} = \frac{\alpha K_T V}{C_V} \qquad \text{... (2)}$$

where α is volume thermal expansivity, K_T is the isothermal bulk modulus, V is volume and C_V is the heat capacity at constant volume. So many researchers[5-18] have reported the relationships for Grüneisen ratio (γ) by using different approaches.

In the present study we have extended the work of Kumar *et al.*[14] by using the concept that C_V changes with increase in compression or pressure. We have tested the validity of present formulation to Mg_2SiO_4. It is known that Mg_2SiO_4 is an important material as well as geophysical mineral[1]. It is one of the few materials for which sufficient data of its properties are available. The wide range of stability in temperature-pressure space and the fact that it is regarded as a major component of the earth layer mantle make Mg_2SiO_4 attractive for the study. Forsterite-rich olivine (Mg_2SiO_4) is the most abundant mineral in the Earth's mantle above depth of about 410 km, where $P \sim 14-15$ GPa[19]. Also, laboratory- synthesized nano-crystalline forsterite has been considered as a possible successor to calcium phosphate bioceramics, due to its exceptionally high fracture toughness[20]. The geophysical importance of forsterite as well as its possible application in medicine justify, in general, a work on the volume dependence of its Grüneisen ratio (γ), since γ is an important parameter in thermodynamics, geophysics, and solid state physics.

2 Method of Analysis

Stacey and Davis[21] have given the following identity:

$$q = \delta_T - K_T' + 1 - \left(\frac{\partial \ln C_V}{\partial \ln V}\right)_T \qquad \text{... (3)}$$

where $\delta_T,\ K_T',\ C_V$ and q are respectively the isothermal Anderson-Grüneisen parameter, first order

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pressure derivative of isothermal bulk modulus and heat capacity at constant volume and second Grüneisen parameter. All these parameters are defined as:

$$\delta_T = -\frac{1}{\alpha K_T}\left(\frac{\partial K_T}{\partial T}\right)_P \quad \text{... (4)}$$

$$K_T' = \left(\frac{\partial K_T}{\partial T}\right)_T \quad \text{... (5)}$$

in which K_T is the isothermal bulk modulus, defined as:

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

and

$$q = \left(\frac{\partial \ln\gamma}{\partial \ln V}\right)_T \quad \text{... (7)}$$

Sharma and Sharma[22] have generalised the isothermal Anderson-Grüneisen parameter in the following manner:

$$\delta_T = \delta_{T_\infty} + \left(\delta_{T_0} - \delta_{T_\infty}\right)\left(\frac{V}{V_0}\right)^m \quad \text{... (8)}$$

where δ_{T_0} and δ_{T_∞} are respectively the values of isothermal Anderson-Grüneisen parameter at zero and infinite pressure, m is a dimensionless adjustable parameter.

Srivastava and Sinha[23] have reported the expression:

$$K_T' = K_\infty' + \left(K_0' - K_\infty'\right)\left(\frac{V}{V_0}\right)^{K_0'} \quad \text{... (9)}$$

where K_0' and K_∞' are the values of first order pressure derivative of isothermal bulk modulus at zero and at infinite pressure. Using Eqs (3, 7–9) we get:

$$\left(\frac{\partial \ln\gamma}{\partial \ln V}\right)_T = \delta_{T_\infty} + \left(\delta_{T_0} - \delta_{T_\infty}\right)\left(\frac{V}{V_0}\right)^m - \left[K_\infty' + \left(K_0' - K_\infty'\right)\left(\frac{V}{V_0}\right)^{K_0'}\right] + 1 - \left(\frac{\partial \ln C_V}{\partial \ln V}\right)_T \quad \text{... (10)}$$

On integration of the above equation, we can get the following equation:

$$\frac{\gamma}{\gamma_0} = \left(\frac{V}{V_0}\right)^{\left(\delta_{T_\infty} - K_\infty' + 1\right)} \times \frac{C_V}{C_{V_0}} \exp\left[A\left(\left(\frac{V}{V_0}\right)^m - 1\right) - B\left(\left(\frac{V}{V_0}\right)^{K_0'} - 1\right)\right] \quad \text{... (11)}$$

where C_{V_0}, γ_0 are respectively the values of specific heat C_V, and Grüneisen parameter at zero pressure and A and B are temperature dependent parameter:

$$A = \left(\frac{\delta_{T_0} - \delta_{T_\infty}}{m}\right) \quad \text{... (12)}$$

$$B = \left(\frac{K_0' - K_\infty'}{K_0'}\right) \quad \text{... (13)}$$

3 Results and Discussion

At infinite pressure, i.e., $P \to \infty$ or $V \to 0$, Eq. (3) becomes:

$$\delta_{T_\infty} = K_\infty' + q_\infty - 1 + C_{T_\infty}' \quad \text{... (14)}$$

Since at infinite pressure, i.e., $P \to \infty$ or $V \to 0$, q_∞ tends to zero[21] and C_{T_∞}' tends to zero[24], now Eq. (14) takes the following form:

$$\delta_{T_\infty} = K_\infty' - 1 \quad \text{... (15)}$$

Following Thomas-Fermi theory[21, 25-28], i.e., $K_\infty' = 5/3$ Eq. (11) results $\delta_{T_\infty} = 2/3$. The values of δ_{T_∞} for both models[21,25-28] satisfy the constraint[29] $0 \langle \delta_{T_\infty} \langle K_\infty'$. We have proposed a simple method to investigate the volume dependence of the Grüneisen ratio (γ) at high temperatures of Mg_2SiO_4 down to a range of volume ratio 0.90.

Using Eq. (15) in Eq.(11) we get:

$$\frac{\gamma}{\gamma_0} = \frac{C_V}{C_{V_0}} \exp\left[A\left(\left(\frac{V}{V_0}\right)^m - 1\right) - B\left(\left(\frac{V}{V_0}\right)^{K_0'} - 1\right)\right] \quad \text{... (16)}$$

where all the parameters are having their as usual meaning.

Recently, Kumar *et al.*[14] reported the following relation for the volume dependence of Grüneisen ratio (γ) by using the concept that C_V remains constant[1]:

$$\frac{\gamma}{\gamma_0} = \exp\left\{\left(\frac{\delta_{T_0} - \delta_{T_\infty}}{m}\right)\left[\left(\frac{V}{V_0}\right)^m - 1\right] - \left(\frac{K_0' - K_\infty'}{K_0'}\right)\left[\left(\frac{V}{V_0}\right)^{K_0'} - 1\right]\right\} \quad \text{... (17)}$$

where all the parameters are having their as usual meaning.

The values of input parameters used in present study are cited in Table 1. The values of C_V are taken from reference[30]. We have investigated the values of volume dependence of the Grüneisen ratio (γ) through Eqs. (16) and (17) for Forsterite. The results obtained through Eqs (16) and (17) are compared with those values calculated by Cynn *et al.*[30] of γ in Table 2. It is found that the results obtained through Eqs (16) and (17) are almost identical to each other and are compatible with those values of γ compiled by Cynn *et al.*[30]. For direct vision we have also plotted the graph for the dependence of Grüneisen ratio (γ) on T at different values of V/V_0 in Fig. 1. Figure 1 reflects that as the temperature increases the values of Grüneisen ratio (γ) decrease and show good agreement with those values of γ compiled by Cynn *et al.*[30] which supports the validity of the present model. It has also been seen that γ changes monotonically above 800 K temperature. It is pertinent that the present paper proposes only a small correction to Eq. (16) from the paper of Kumar *et al.*[14]. This correction is reduced to the C_{V_0}/C_V multiplier on the right side of Eq. (16) from the present study. It is readily seen from Table 2 of Cynn *et al.*[30] that C_V practically does not vary with pressure. Therefore, the multiplier $C_{V_0}/C_V \sim 1$ and does not influence the change of γ/γ_0 with V/V_0 in the studied range of compression ratios. Also, V/V_0 influences the results very slightly because of the very

Table 1 – Values of input parameters for Mg_2SiO_4 used in calculations

T(K)	δ_{T_0} [1]	K_0' [1]	γ_0 [1]	C_{V_0} (J/gK)[30]	m[31]
300	5.940	5.370	1.290	0.8324	2.380
400	5.580	5.400	1.210	0.9760	2.240
500	5.490	5.440	1.180	1.0482	2.210
600	5.480	5.470	1.170	1.0929	2.190
700	5.490	5.500	1.160	1.1244	2.140
800	5.470	5.540	1.150	1.1480	2.100
900	5.460	5.570	1.150	1.1669	1.980
1100	5.460	5.630	1.140	1.1972	1.660
1200	5.490	5.670	1.150	1.2095	1.270
1300	5.440	5.700	1.150	1.2205	1.240
1600	5.400	5.800	1.140	1.2489	1.240

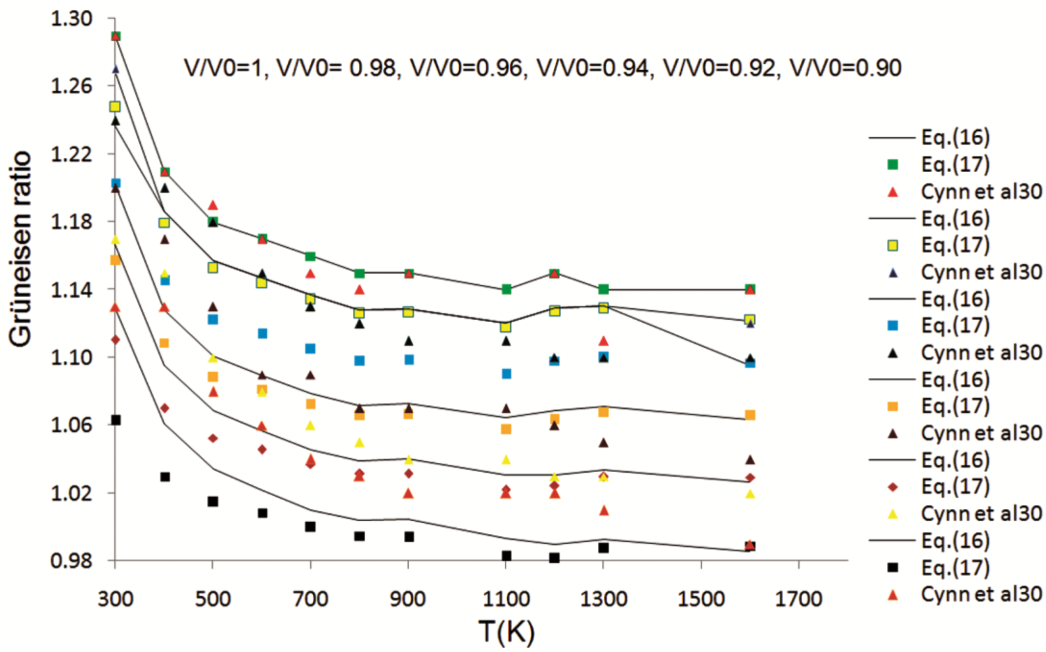

Fig. 1 – Values of Grüneisen ratio (γ) of Mg_2SiO_4 as a function of temperature at different volume ratios calculated here with Cynn *et al.*[30]

Table 2 – Grüneisen ratio (γ) of Mg_2SiO_4 as a function of volume ratio and temperature calculated through (a) Eq. (16), (b) Eq. (17) and (c) Cynn *et al.*[30]

$T(K)$	$\frac{V}{V_0} = 1.0$			$\frac{V}{V_0} = 0.98$			$\frac{V}{V_0} = 0.96$			$\frac{V}{V_0} = 0.94$			$\frac{V}{V_0} = 0.92$			$\frac{V}{V_0} = 0.90$		
	γ			γ			γ			γ			γ			γ		
	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)
300	1.29	1.29	1.29	1.27	1.25	1.27	1.24	1.20	1.24	1.20	1.16	1.20	1.17	1.11	1.17	1.13	1.06	1.13
400	1.21	1.21	1.21	1.19	1.18	1.20	1.19	1.15	1.20	1.13	1.11	1.17	1.10	1.07	1.15	1.06	1.03	1.13
500	1.18	1.18	1.19	1.16	1.15	1.18	1.16	1.12	1.18	1.10	1.09	1.13	1.07	1.05	1.10	1.03	1.01	1.08
600	1.17	1.17	1.17	1.15	1.14	1.15	1.15	1.11	1.15	1.09	1.08	1.09	1.06	1.05	1.08	1.02	1.01	1.06
700	1.16	1.16	1.15	1.14	1.13	1.13	1.14	1.11	1.13	1.08	1.07	1.09	1.05	1.04	1.06	1.01	1.00	1.04
800	1.15	1.15	1.14	1.13	1.13	1.12	1.13	1.10	1.12	1.07	1.07	1.07	1.04	1.03	1.05	1.00	0.99	1.03
900	1.15	1.15	1.15	1.13	1.13	1.11	1.13	1.10	1.11	1.07	1.07	1.07	1.04	1.03	1.04	1.00	0.99	1.02
1100	1.14	1.14	1.02	1.12	1.12	1.11	1.12	1.09	1.11	1.06	1.06	1.07	1.03	1.02	1.04	0.99	0.98	1.02
1200	1.15	1.15	1.15	1.13	1.13	1.10	1.13	1.10	1.10	1.07	1.06	1.06	1.03	1.02	1.03	0.99	0.98	1.02
1300	1.14	1.14	1.11	1.13	1.13	1.10	1.13	1.10	1.10	1.07	1.07	1.05	1.03	1.03	1.03	0.99	0.99	1.01
1600	1.14	1.14	1.14	1.12	1.12	1.12	1.10	1.10	1.10	1.06	1.07	1.04	1.03	1.03	1.02	0.99	0.99	0.99

narrow range, it varies in. Thus the Eq. (16) is an asymptotic approximation of Eq. (17) in the limit of $P \rightarrow \infty$ or $V \rightarrow 0$.

4 Conclusions

We have proposed a simple and straight forward empirical relationship to estimate the values of volume dependence of Grüneisen ratio (γ) for Mg_2SiO_4 down to a range of volume ratio 0.90. It is found that the results obtained through Eq. (16) are in good agreement with those values of γ compiled with Cynn *et al.*[30]. Compatibly of results obtained in the present study with values of γ compiled by Cynn *et al.*[30] shows the validity of the present model. Results thus obtained through Eqs (16) and (17) are identical to each other. Henceforth, the Eq. (16) is an asymptotic approximation of Eq. (17). There is no significant effect of heat capacity on Grüneisen ratio (γ). However, this requires further investigations that heat capacity influences the values of volume dependence of Grüneisen ratio (γ). It may be studied in future for those materials that have data on C_V and γ at high temperatures and high pressures.

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