PRAMANA
— journal of
physics

Vol. 76, No. 1
January 2011
pp. 183–188

Thermoelastic properties of minerals at high temperature

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MS received 1 April 2010; revised 7 May 2010; accepted 8 June 2010

Abstract. The knowledge of elasticity of the minerals is useful for interpreting the structure and composition of the lower mantle and also in seismic studies. The purpose of the present study is to discuss a simple and straightforward method for evaluating thermoelastic properties of minerals at high temperatures. We have extended the Kumar's formulation by taking into the account the concept of anharmonicity in minerals above the Debye temperature (θ_{D}). In our present study, we have investigated the thermophysical properties of two minerals (pyrope-rich garnet and $MgAl_2O_4$) under high temperatures and calculated the second-order elastic constant (C_{ij}) and bulk modulus (K_{T}) of the above minerals, in two cases first by taking Anderson–Gruneisen parameter (δ_{T}) as temperature-independent and then by treating δ_{T} as temperature-dependent parameter. The results obtained when δ_{T} is temperature-dependent are in close agreement with experimental data.

Keywords. Elastic constants; bulk modulus; minerals.

PACS Nos 91.60.Fe; 91.60.Gf; 91.60.Ba

1. Introduction

Elastic constants and their variations with temperature provide useful insight into the nature of interatomic forces. Elastic properties of materials at high pressure and high temperature are of great interest to researchers in many fields, such as physical sciences, earth sciences, and material sciences. In the present study, a simple and straightforward model theory was used to analyse the elastic constants of pyrope-rich garnet and $MgAl_2O_4$. This theory is independent of crystal potential and thus does not involve any potential parameters.

Pyrope is the only member of the garnet family which always displays red colouration in natural samples, and because of this characteristic it got its name. The composition of pure pyrope is $Mg_3Al_2(SiO_4)_3$, although other elements are present in minor proportions. These other elements include Ca, Cr, Fe and Mn. Suzuki and Anderson calculated C_{ij} for pyrope-rich garnet over the temperature range 298–993 K at irregular intervals of T. The

specimen used by Suzuki and Anderson was a single-crystal natural garnet with composition: pyrope, 72.6%; almandine, 15.7%; uvarovite, 6.1%; androdite, 4.3%; spessartine, 0.7%; and grossular, 0.6% [1].

The class of oxide minerals includes those minerals in which the oxide anion (O^{2-}) is bonded to one or more metal ions. The spinels are another class of minerals of the general formula of $A^{2+}B_2^{3+}O_4^{2-}$ which crystallize in the cubic (isometric) crystal system, with the oxide anions arranged in a cubic close-packed lattice and the cations A and B occupying some or all of the octahedral and tetrahedral sites in the lattice. A common example of a normal spinel is $MgAl_2O_4$ [2,3]. Cynn calculated C_{ij} for single-crystal $MgAl_2O_4$ over the range 298–999 K at irregular intervals of T up to 1060 K, but a sudden change in the slope of the data near 1000 K is attributed to cation disordering [4]. To analyse the temperature dependency of elastic constants and their combinations, different relations based on thermodynamic parameters are proposed in [5,6].

The relations for predicting the temperature dependency of elastic constants given in [7,8] are well-known and widely used. The relations given by Suzuki *et al* [7] required heavy computational work. Although these relations predict good results for variation of volume, for elastic constants the predictions are not good. This relation has further been simplified by Singh and Kumar [8] by considering the volume dependency of Anderson–Gruneisen parameter (δ_{T}) in their thermodynamic analysis. They ignored the higher-order terms, i.e. anharmonic terms, in the expansion of the logarithmic series of the volume change and so the results obtained by these workers are not good.

In the present work we have considered the anharmonic terms and also the temperature dependency of the Anderson–Gruneisen parameter (δ_{T}) as this concept was assumed by Singh and Gupta [9] to explain the thermoelastic properties of MgO crystal. We have calculated the second-order elastic constant (SOEC) (C_{ij}) and bulk modulus (K_{T}) of pyrope-rich garnet and $MgAl_2O_4$, first by taking Anderson–Gruneisen parameter (δ_{T}) as temperature-independent and then by taking δ_{T} as temperature-dependent.

2. Method of analysis

The anharmonicity of the lattice vibration is generally due to thermal expansion in solids. The interatomic separation increases on increasing the temperature of the solid. In the present work we have used the modified Kumar equation, in which the anharmonic term in the expansion of logarithmic series of the volume change with temperature is considered.

Kumar reported a relation for the relative volume change V/V_0 as a function of temperature under thermal pressure, using the theory of high pressure and high temperature [10]. At $P = 0$, this relation leads to

$$\frac{V}{V_0} - 1 = -\frac{1}{B_0' + 1} \ln\left[1 - \alpha_0 \left(B_0' + 1\right)\left(T - T_0\right)\right], \tag{1}$$

where α_0 is the thermal expansion coefficient at T_0 and B_0' is the first pressure derivative of the bulk modulus, which can be assumed to be $\simeq \delta_{\mathrm{T}}$ as mentioned in [11–14]. Kumar's formulation is limited up to the harmonic expansion of the logarithmic series while he has ignored the higher-order terms. At high temperature, to understand the elastic behaviour

of solids, it is necessary to include the anharmonic terms. To explain the anharmonic elastic behaviour of solids, we include the higher-order terms in the expansion of logarithmic series, i.e. the anharmonic terms,

$$\frac{V}{V_o} - 1 = \frac{1}{A}\left[\acute{e}^{\alpha_0 A(T-T_0)} - 1 + \frac{\{\alpha_0 A\,(T-T_0)\}^3}{6}\right], \tag{2}$$

where A is a constant at $P = 0$, $V = V_0$ and $\delta_{\mathrm{T}} = \delta_{\mathrm{T}}^0$ and given as $A = \delta_{\mathrm{T}}^0 + 1$.

Differentiating eq. (2) with respect to T and using standard definition of α, we have finally obtained the following expression:

$$\frac{\alpha}{\alpha_0} = \frac{\mathrm{e}^{\alpha_0 A(T-T_0)} + \frac{\{\alpha_0 A(T-T_0)\}^2}{2}}{1 + \frac{1}{A}\left[\mathrm{e}^{\alpha_0 A(T-T_0)} - 1 + \frac{\{\alpha_0 A(T-T_0)\}^3}{6}\right]}\,. \tag{3}$$

Now assume that the product of thermal expansivity and bulk modulus will remain constant. The expression for bulk modulus as a function of temperature can be written as

$$\frac{K}{K_{T_0}} = \frac{1 + \frac{1}{A}\left[\mathrm{e}^{\alpha_0 A(T-T_0)} - 1\frac{\{\alpha_0 A(T-T_0)\}^3}{6}\right]}{\mathrm{e}^{\alpha_0 A(T-T_0)} + \frac{\{\alpha_0 A(T-T_0)\}^2}{2}}\,. \tag{4}$$

Thus, on generalizing eq. (4), the equation for SOEC can be expressed as

$$\frac{C_{ij}}{C_{0ij}} = \frac{1 + \frac{1}{A}\left[\mathrm{e}^{\alpha_0 A(T-T_0)} - 1\frac{\{\alpha_0 A(T-T_0)\}^3}{6}\right]}{\mathrm{e}^{\alpha_0 A(T-T_0)} + \frac{\{\alpha_0 A(T-T_0)\}^2}{2}}, \tag{5}$$

where C_{ij} represent any of the elastic moduli as C_{11}, C_{12}. In these equations A should vary according to the selected elastic moduli. Here $A = (\delta_{0ij} + 1)$ and δ_{0ij} can be evaluated using the method discussed in [14].

We have considered the temperature dependence of δ_{T} as the empirical formula [9]

$$\delta_{\mathrm{T}} = \delta_{\mathrm{T}}^0 X^k, \tag{6}$$

where δ_{T}^0 is the Anderson–Gruneison parameter at $T = T_0$, and $X = (T/T_0)$, T_0 is the reference temperature, k is the new dimensionless parameter which can be calculated

Table 1. Input parameter for pyrope-rich garnet and $MgAl_2O_4$ respectively at room temperature, α_0 (10^{-6} K^{-1}) and K_{T}, C_{ij} (10^{10} Pa) [5].

Parameter	α_0	K_{T}	k	C_{11}	C_{12}	C_{44}
Pyrope-rich garnet	21.1	20.79	0.018	29.66	10.85	9.16
$MgAl_2O_4$	23.6	16.94	0.039	29.22	16.87	15.65

Table 2. Values of δ_{T} and δ_{0ij} at room temperature for pyrope-rich garnet and $MgAl_2O_4$ respectively [5].

Parameter	δ_{T}	δ_{011}	δ_{012}	δ_{044}
Pyrope-rich garnet	6.27	5.71	7.03	3.70
$MgAl_2O_4$	7.73	6.81	8.43	9.08

Table 3. Values of K_{T} (in units of 10^{10} Pa) calculated from eq. (4) as a function of temperature with experimental data [5] for pyrope-rich garnet.

	Calculated in the present study		
	When δ_{T} is independent of temp.	When δ_{T} depends on temp.	Experimental
Temperature	K_{T}	K_{T}	K_{T}
300	16.94	16.94	16.94
400	16.7	16.69	16.65
500	16.47	16.44	16.40
600	16.23	16.19	16.14
700	16.00	15.94	15.91
800	15.76	15.69	15.66
900	15.53	15.43	15.41
1000	15.3	15.19	15.16

Table 4. Values of K_{T} (in units of 10^{10} Pa) calculated from eq. (4) as a function of temperature with experimental data [5] for $MgAl_2O_4$.

	Calculated in the present study		
	When δ_{T} is independent of temp.	When δ_{T} depends on temp.	Experimental
Temperature	K_{T}	K_{T}	K_{T}
300	20.79	20.79	20.79
400	20.49	20.45	20.46
500	20.2	20.11	20.08
600	19.9	19.77	19.78
700	19.61	19.43	19.44
800	19.32	19.09	19.09
900	19.03	18.76	18.73
1000	18.74	18.42	18.44

Table 5. Values of C_{11}, C_{12} and C_{44} (in units of 10^{10} Pa) calculated from eq. (5) as a function of temperature with experimental data [5] for pyrope-rich garnet.

	Calculated in the present study								
	When δ_{T} is independent of temp.			When δ_{T} depends on temp.			Experimental		
Temperature	C_{11}	C_{12}	C_{44}	C_{11}	C_{12}	C_{44}	C_{11}	C_{12}	C_{44}
300	29.66	10.85	9.16	29.66	10.85	9.16	29.66	10.85	9.16
400	29.26	10.67	9.08	29.28	10.68	9.08	29.27	10.69	9.08
500	28.86	10.49	9.01	28.91	10.51	8.99	28.92	10.59	9.00
600	28.46	10.31	8.93	28.53	10.34	8.91	28.55	10.46	8.91
700	28.06	10.13	8.85	28.16	10.18	8.83	28.21	10.37	8.83
800	27.66	9.95	8.78	27.79	10.01	8.75	27.85	10.26	8.74
900	27.26	9.77	8.7	27.42	9.84	8.67	27.48	10.15	8.65
1000	26.86	9.59	8.63	27.04	9.68	8.59	27.12	10.03	8.55

Table 6. Values of C_{11}, C_{12} and C_{44} (in units of 10^{10} Pa) calculated from eq. (5) as a function of temperature with experimental data [5] for $MgAl_2O_4$.

	Calculated in the present study								
	When δ_{T} is independent of temp.			When δ_{T} depends on temp.			Experimental		
Temperature	C_{11}	C_{12}	C_{44}	C_{11}	C_{12}	C_{44}	C_{11}	C_{12}	C_{44}
300	29.22	16.87	15.65	29.22	16.87	15.65	29.22	16.87	15.65
400	28.8	16.57	15.35	28.86	16.61	15.39	28.86	16.63	15.53
500	28.37	16.27	15.05	28.49	16.35	15.13	28.44	16.37	15.36
600	27.95	15.97	14.75	28.12	16.09	14.87	28.11	16.19	15.22
700	27.53	15.67	14.45	27.76	15.83	14.61	27.72	15.98	15.07
800	27.12	15.37	14.16	27.4	15.57	14.35	27.33	15.77	14.92
900	26.7	15.07	13.86	27.03	15.32	14.1	26.92	15.55	14.77
1000	26.29	14.79	13.57	26.67	15.06	13.84	26.60	15.40	14.61

from the slope of the graph plotted between log δ_{T} and log(T/T_0). So the value of k is defined as

$$k = \frac{\partial \ln \delta_{\mathrm{T}}}{\partial \ln X}\,. \tag{7}$$

Using eqs (4) and (5) we can calculate the bulk modulus and second-order elastic constant (SOEC) of the minerals at high temperature.

3. Results and discussion

In the present study, we used the potential-independent model, in which the equation of state (EOS) was modified using the concept of thermal pressure ($P_{\rm th}$) and by taking into account the anharmonic term in the expansion of logarithmic series for volume variation with temperature. The anharmonic term arises because of the thermal expansion. In this work, we have just extended the Kumar's formulation by taking into the account the concept of anharmonicity produced in minerals above the Debye temperature ($\theta_{\rm D}$). Using eqs (4) and (5), we have thus calculated the value of bulk modulus ($K_{\rm T}$) and second-order elastic constants (SOEC) (C_{ij}) of the pyrope-rich garnet and $MgAl_2O_4$, first by taking $\delta_{\rm T}$ as a temperature-independent parameter and then by treating $\delta_{\rm T}$ as a temperature-dependent parameter suggested by Singh and Gupta [9].

The values of input parameters are given in tables 1 and 2 with the corresponding references. The calculated results in both cases are given with available experimental data for bulk modulus ($K_{\rm T}$) in tables 3 and 4 and second-order elastic constants C_{11}, C_{12} and C_{44} in tables 5 and 6 for pyrope-rich garnet and $MgAl_2O_4$ respectively. It is evident from tables 3–6 that the calculated values in the second case, in which $\delta_{\rm T}$ is temperature-dependent are in good agreement with the experimental value. It proves that the Anderson–Gruneisen parameter ($\delta_{\rm T}$) strongly depends on temperature. The good agreement between the calculated and experimental values of elastic constants at higher temperature for minerals also reveals the validity of the relationship used in the present study.

References

[1] I Suzuki and O L Anderson, *J. Phys. Earth* **31**, 125 (1983)
[2] Z P Chang and G R Barsch, *J. Geophys. Res.* **78**, 2418 (1973)
[3] R F S Hearmon, *Landolt–Birnstein tables* edited by IIellwege and AM Hellwege (Springer-Verlag, Berlin, 1979) pp. l–244
[4] H Cynn, *Effects of cation disordering in $MgAl_2O_4$ spinel on the rectangular parallelepiped resonance and Raman measurements of vibrational spectra*, Ph.D. thesis (University of California, Los Angeles, 1992), 169 pp.
[5] O L Anderson and D G Issak, *Min. Phys. Crystallogr.* **2**, 64 (1995)
[6] O L Anderson, *Equation of states of solids for geophysics and ceramic sciences* (Oxford University Press, Oxford, 1995)
[7] I Suzuki, S Okajima and K Seya, *J. Phys. Earth* **27**, 63 (1979)
[8] P P Singh and M Kumar, *Physica* **B344**, 41 (2004)
[9] K Y Singh and B R K Gupta, *Physica* **B334**, 226 (2003)
[10] M Kumar, *Physica* **B222**, 229 (1995)
[11] A Chopelas and R Boehler, *Geophys. Res. Lett.* **16**, 1347 (1989)
[12] O L Anderson and D G Issak, *J. Phys. Chem. Solids* **54**, 221 (1993)
[13] A Vijay, *Physica* **B349**, 62 (2004)
[14] M Singh, P P Singh, B R K Gupta and M Kumar, *High Temp. High Press.* **33**, 199 (2001)