

EQUATION OF STATE OF GROSSULAR GARNET: A REVIEW

¹Abhishek Kamboj, ²Santosh Mehta, ³Suneeta Singh, ⁴Bhupendra Singh Rawat

^{1,2}Scholar, ³Assistant Professor, ⁴Associate Professor

^{1,2,3,4}Department of Physics, UCALS, Uttarakhand University, Dehradun, India

Abstract: Grossular Garnet (Hessonite) is a common formulation of Grossular with chemical formula $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$. Its chemical composition consists of Calcium (26.69%), Aluminium (11.98%), Silicon (18.71%) and Oxygen (42.62%). Its color ranges from light to dark yellow to reddish brown, light to dark green, sometimes translucent to opaque pink. It is also but rarely found in colorless form. It has a cubic crystal system belonging to hexoctahedral class. It is found below the earth's surface in contact metasomatic deposits. Studying the equation of state allows us to observe the chemical properties of a material. The study of equation of state of grossular garnet allows us to observe its properties like compressibility, thermal properties, relation between pressure and volume, elastic parameters.

Index terms: Grossular garnet, Thermal expansion, In situ X-ray diffraction, High-pressure, Single-crystal diffraction, Bulk modulus, Thermoelastic parameters, Compressibility.

I. INTRODUCTION

Garnets form a fundamental component of the earth's upper mantle - change zone and accept an essential occupation in petrogenetic forms of high temperature and high pressure. Garnets are likewise imperative segments of subducted oceanic crust. Grossular is the most varicolored of the Garnets. The term Garnet depicts a gathering name for a few firmly related minerals that structure vital gemstones. The substance equation for grossular garnet is $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$. Grossular Garnet is found in contact transformed limestones with vesuvianite, diopside, wollastonite and wernerite. A derivative of grossular namely hydrogrossular is used as carving gemstone.

The equation of state relates the volume V , temperature T and pressure P in the state of thermodynamic equilibrium $f(P,V,T)=0$. An Equation of State (EOS) is a semi-exact useful connection between pressure, volume and temperature of an unadulterated substance. It is a thermodynamic condition depicting the condition of matter under a given arrangement of physical conditions. Most EOS's are semi-experimental and are commonly produced for unadulterated substances. Their application to mixtures requires an extra factor (structure) and thus a proper mixing rule.

A well characterized EOS gives the chance to ascertain various thermodynamic properties with the utilization of constrained experimental data. Boyle's law (1662) was perhaps the first expression of the equation of state. Mie-Gruniesen and Birch-Murnaghan, are the most famous EOS's for solids. In 1903, Gustav Mie developed an intermolecular potential to derive high temperature solid state equations. In 1912, Eduard Gruniesen extended Mie's model to below Debye's temperature, which gave rise to the state equation of Mie - Gruniesen. Murnaghan exhibited in 1944 an EOS that depended on the principle of conservation of mass, Hooke's law for little varieties of stress and a presumption that the bulk modulus was direct regarding pressure. This suspicion has been demonstrated precise at low pressure by examination with experimental data (Wedepohl 1976). Murnaghan's EOS is as yet utilized today and has additionally been created by broadening the estimate for the bulk modulus to higher order Taylor expansion with pressure (Fuchizaki 2006). The second order form has been alluded to as the altered Murnaghan equation (Birch 1986). The higher order approximations give progressively muddled counts. What's more? It is hard to tentatively decide the higher order derivatives of the bulk modulus. The experimental edge of the penumbra is now defined by the second derivative of the bulk modulus (Anderson 1995). In this manner, the most widely recognized form is still truncation at the direct term.

Commonly used equation of state's are described below:

- In his theory of finite strain, Murnaghan noted that K is linear in P to a good approach to high compressions.

$$P(V) = \frac{K_0}{K'_0} \left[\left(\frac{V}{V_0} \right)^{-K'_0} - 1 \right]$$

where, K_0 is the modulus of incompressibility, K'_0 is its derivative with respect to pressure.

- The Birch-Murnaghan isothermal state equation is a relation between the body's volume and the pressure it is subjected to. It can be expressed as,

$$P(V) = \frac{3B_0}{2} \left[\left(\frac{V_0}{V} \right)^{\frac{7}{3}} - \left(\frac{V_0}{V} \right)^{\frac{5}{3}} \right] \left\{ 1 + \frac{3}{4} (B'_0 - 4) \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right] \right\}$$

where, V denotes the deformed volume, P denotes the pressure, B_0 denotes the bulk modulus, V_0 denotes the reference volume and B'_0 denotes the derivative of the bulk modulus with respect to pressure.

- In 1903, Gustav Mie developed a potential for intermolecular derivations of high-temperature solid state equations. In 1912, Mie's model was extended by Eduard Grüneisen to temperatures below the Debye temperature at which quantum effects became significant. It is possible to express the Grüneisen model in the form,

$$\Gamma = V \left(\frac{dp}{de} \right)_v$$

where p denotes the pressure, V denotes the volume, Γ denotes the Grüneisen parameter and e denotes the internal energy which represents the thermal pressure from a set of vibrating atoms.

- The integrated Grüneisen model can be expressed as,

$$p - p_0 = \frac{\Gamma}{V} (e - e_0)$$

where e_0 and p_0 denotes the internal energy and pressure at a state with temperature 0K.

- The state equation Mie-Grüneisen is a relationship of pressure and solid's volume at a certain temperature. It is used in a shock compressed solid for determining the pressure. The relationship between the Mie-Grüneisen is a unique form of the Grüneisen model that describes the effects of vibrational change in crystal lattice volumes. Many variations of the state equation Mie - Grüneisen state equation are being used. Grüneisen model can be expressed as a general form,

$$p = \frac{\rho_0 C_0^2 \chi \left[1 - \frac{\Gamma_0}{2} \chi \right]}{(1 - s\chi)^2} + \Gamma_0 E; \quad \chi := 1 - \frac{\rho}{\rho_0}$$

where ρ_0 denotes the initial density, ρ denotes the current density, C_0 denotes the bulk speed of sound, Γ_0 denotes Grüneisen's gamma at the reference state, $s = dU_s/dU_p$ denotes a linear Hugoniot slope coefficient, U_p denotes the particle velocity, U_s denotes the shock wave velocity and E denotes the internal energy per unit reference volume.

II. Review of literature:

Donald G. Isaak, Hitoshi Oda and Orson L. Anderson (1992): New high temperature elasticity data were presented on two grossular garnet specimens. One specimen was single crystal; the other was polycrystalline with approximately 22 percent of molar andradite. Their data extended the high temperature regime from 1000 to 1350 K and the compositional range of temperature data to near-endmember grossular. They also presented new data on calcium-rich garnet's thermal expansiveness. There were no differences in temperature T derivatives of isotropic bulk K 's and shear moduli on comparing results between these two specimens at ambient conditions. Most elastic moduli were observed with small, but measurable, nonlinear temperature dependencies. With the new data, several dimensional parameters had been calculated and used to demonstrate the effects of various assumptions on elastic state equations interpolate to high temperatures. Their results had to do with the amount of diopside needed to explain the gradients of shear velocity in the transition zone of Earth.

Steeve Gréaux et al. (2010): The thermoelastic parameters of synthetic $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (Grossular Garnet) were investigated in situ using the kawai type multi-anvil press apparatus combined with synchrotron radiation at high-pressure and high-temperature by energy dispersive X-ray diffraction. Measuring was carried out with pressures of up to 20 GPa and temperatures of up to 1,650 K: the entire high P-T stability field of grossular garnet covered this P-T range. The thermoelastic parameters are given by fitting their P-V-T data with the high-temperature third order Birch-Murnaghan or the Mie-Grüneisen-Debye thermal state equations. By comparing the two approaches, the bulk modulus of grossular garnet was proposed to be restricted.

Yoshio Kono et al. (2010): A study has been carried out in which simultaneous measurements of ultrasonic elastic wave velocity and in situ X-ray synchrotron on grossular garnets were performed with up to 1650 K and 17 GPa. These figures produced a pressure derivative of the bulk modulus and shear modulus, which were in good coordination with garnets with varying chemical compositions. The bulk modulus of the grossular has similar temperatures dependence to that of other garnets, while the temperature dependence of the shear modulus of grossular is higher than that of the magnesium-end-group garnets.

Kenji Kawai and Taku Tsuchiya (2012): Temperature and pressure effects of grossular garnet were investigated by the first principle's computation method in 2012 and it was found to dissociate into an array of CaSiO_3 Ca-perovskite (Pv) and Al_2O_3 Corundum (Cor) with jumps in compression wave (8.0 percent), shear wave (11.6 percent) and mass sound velocity (5.9 percent) and velocity (12.1 perceived) at approximately 23.4 GPa. By adapting data to the Birch-Murnaghan third-order equation, the equation of state parameters (zero pressure bulk modulus B_0 and its B_0 's pressure derivation) were determined. The B_0 and B_0 parameters were well in line with the experimental data.

Wei Du et al. (2015): A study had been carried out using synchrotron X-ray powder diffraction, measuring unit cell parameters of pyrope, grossular and four intermediate compositions of a series of synthetic garnets to approx. 900 K and 10 GPa. The thermal expansion coefficients of pyrope-grossular garnets increase evenly with temperature. Values for the two end members grossular and pyrope are the same. The Bulk modulus of grossular K_0 (with fixed K_0' , the pressure derivative of the bulk modulus) and bulk modulus of pyrope K_0 (with fixed K_0') were shown to be compatible with previously reported values using a third order the Birch-Murnaghan state equation. The compositional dependence of the thermal expansion is similar to the compositional dependence of bulk modulus. Excess volumes were found to be relatively large in pyrope-grossular series at even high pressures (~6GPa) and temperatures (~800 K), supporting the observation of crystal-exsolution in this garnet join.

S. Milani et al. (2017): A study had been conducted on thermoelastic behavior of grossular garnet at high pressure and temperature and the results were divided into four sets of data: Temperature-Volume data, Temperature-Volume-Bulk Modulus data, Pressure-Volume data and P-V-T-K and PVT equation of state. This data was analyzed and the results were obtained. A constant increase in cell volume is observed with dependence on temperature without evidence of irreversible changes. T-V data and T-K's data from Isaak et al.(1992) of grossular yielded identical results as those obtained from T-V-K data. This implies that the

assumption γ is a constant is reasonably valid. With increased pressure up to a maximum hydrostatic pressure of 7.5 GPa, the grossular's unit cell volume decreases smoothly. This pressure covers the upper mantle stability pressure range.

Jay D. Bass et al. (1989): In its phases, a garnet structure is most likely to carry aluminum. Thus the elastic properties of the garnet have stood interesting to constrain the composition of earth's mantle. The grossular (Gr) was simply labelled "pastel grossular" and is of unknown origin.

Grossular appearance and infrared (IR) spectrum are similar to that of Kenya and Tanzania African specimens (G. Rossman, personal communication, 1988). Grossular garnet elastic module estimates properties such as lattice parameter, refractive index and density from several recent studies. The elastic moduli of grossular garnet estimate the properties like lattice parameter, refractive index and density from several recent studies. A hydrogrossular component would decrease the refractive index and increase the lattice parameter of grossular relative to the pure grossular end-member; no evidence was found for an appreciable hydrous component on the basis of the measurements. The single crystal elastic properties of the grossular at 1 atm. pressure and 22^oC temperature by Brillouin spectroscopy are accurate within better than $\pm 1\%$ except for mixed moduli.

B.J. Hensen et al (1975): The attributes of mixed garnet solid solutions had been studied by many authors and some have experimental evidences. Garnet's compositional activity relationships are of major interest in understanding the coefficient of activity and the coefficient of interaction of the grossular garnet. Values of activity coefficient for garnets had been obtained at 1000^o, 1100^o, 1200^o and 1300^oC with 10-12 mole percent of grossular at pressures between 15 and 21 Kb. This data is compatible with Grossular-pyrope solid solutions in the regular solid model. The parameter of interaction (W) is inversely proportional to the temperature and is given in cal (T in K) with $W = 7460 - 4.3 T$. A major positive deviation from ideality is shown in the pyrope-grossular solid solutions.

Mu chi and J. Michael Brown (1997) et al: Laser - induced phonon spectroscopy was used to determine the elastic constants and state equation at a temperature of 25^o C of a natural garnet at 20 GPa pressure. The moduli of garnet linearly changes with pressure. The shear modulus in GPa is $94.7 + 1.76P$ and the adiabatic bulk modulus is given by $K = 170.8 + 4.09P$. At constant density, the derivative of the shear modulus with respect to temperature is derived from the temperature and pressure dependencies of the elastic constants. Murnaghan equation with $p_0 = 3.810 \text{ g/cm}^3$, $KT = 169.5 \text{ GPa}$, $K' = 4.09$, i.e. $p = 3.810 (1 + 0.024 p)$ described the pressure dependence of density. All elastic constants of a pyrope rich garnet are linear in accordance with pressure within experimental limits of 20Gpa. The density dependence of the bulk modulus is estimated to be 32 percent lower at 20 GPa. The shear modulus has a very small constant density derivative of temperature at 1 bar.

Suzuki and Anderson (1983) et al: the constant pressure derivatives had been reported and the coefficients of thermal expansion at 298 K and 1 bar, $\alpha = 2.55 \times 10^{-5} \text{ K}^{-1}$ and at 993 K, $3.31 \times 10^{-5} \text{ K}^{-1}$. At 20 GPa thermal expansion is reduced 32% from its 1 bar value. The most prominent attribute of the data shows that the tabulated derivatives depend on small pressure and temperature.

Robert M. Hazen and Larry W. Finger (2008) et al: The variations had been studied that the physical properties of garnet with pressure and structure helps in framing the model of earth's interior. On the basis of empirical compression equation, Hazen suggested a silicon tetrahedral modulus of 8000 kbar. Pyrope shows an inverse relation to temperature and pressure between structural changes. Based on three dimensional crystal X ray data, the crystal structure and compressibility of the end member garnets pyrope (synthetic $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ at 1 bar and 16, 31, 43 and 56 kbar) and the grossular (natural $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ at 1 bar and 19, 35 and 61 kbar) were calculated. Cubic unit-cell dimensions for pyrope are $a = 11.456$ at 1 bar and 11.332A at 50 kbar; for grossular a 11.846A at 1 bar and 11.720A at 50 kbar. Bulk modulus of pyrope and grossular are about 1350 kbar which is consistent, but significantly lower than elastic constant data with previous static compression data.

Table 1. Comparison of lattice parameters of grossular garnet at ambient P, T conditions

SN	Grossular Composition	$V_0(\text{Å}^3)$	References
1.	Synthetic $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	1661.6(1)	Steeve Gréaux et al. (2010)
2.	$(\text{Ca}_{2.96}\text{Mn}_{0.04})(\text{Al}_{1.95}\text{Fe}_{0.05})\text{Si}_3\text{O}_{12}$	1661.9(4)	Novak and Gibbs (1971)
3.	$(\text{Ca}_{2.96}\text{Mn}_{0.04})(\text{Al}_{1.95}\text{Fe}_{0.05})\text{Si}_3\text{O}_{12}$	1662.3(8)	Meagher (1975)
4.	Natural $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	1664.2(2)	Sawada (1999)
5.	Synthetic $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	1664.1(2)	Rodehorst et al. (2002)
6.	Synthetic $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	1664 (2)	Yoshio Kono et al. (2010)
7.	$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} + 0.5 \text{ wt}\% \text{ FeO}$	1662.3(4)	Hazen and Finger (1978)
8.	Natural $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	1660.2(3)	Zhang et al (1999)
9.	$(\text{Ca}_{2.95}\text{Mg}_{0.04}\text{Fe}_{0.01})(\text{Al}_{1.97}\text{Ti}_{0.02}\text{Mn}_{0.01})\text{Si}_{2.99}\text{O}_{12}$	1663.6	Conrad et al. (1999)
10.	$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	1666.9	Nobes et al. (2000)
11.	$(\text{Ca}_{2.90}\text{Fe}_{0.10})(\text{Al}_{1.95}\text{Ti}_{0.04}\text{Mn}_{0.01})\text{Si}_{2.99}\text{O}_{12}$	1666.4(4)	Pavese et al. (2000)

*Numbers in parenthesis represent the relative error calculated for V_0

* V_0 denotes unit cell volume

III. Conclusion:

Through various studies, by applying certain parameters like constraining the pressure range, temperature range, various data was obtained regarding the bulk moduli, thermoelastic parameters, compressibility, thermal expansion of the grossular garnet. Studies found that most of the elastic moduli had small and concurrent temperature dependencies. S-wave velocities and bulk and shear modulus showed linear dependence on pressure and temperature. Coefficients of thermal expansion of grossular garnets uniformly increase with temperature. The compositional dependence of thermal expansion resembles the compositional dependence of bulk modulus. The unit cell volume constantly increases depending on temperature without evidence of an irreversible change. The unit cell volume of grossular decreases smoothly with increasing pressure upto a maximum hydrostatic pressure equivalent to that of the upper mantle range. From several recent studies, it was found that the elastic moduli of grossular garnet estimate the properties like lattice parameter, refractive index and density.

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